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Tank 241-T-111 Characterization Report

Brett C. Simpson
Westinghouse Hanford Company, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-87RL10930

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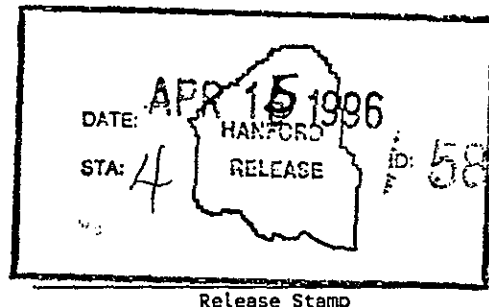
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Tank 241-T-111 Characterization Report

B. C. Simpson

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March 1996

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management



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EXECUTIVE SUMMARY

Single-shell tank 241-T-111 is a Hanford Site High-Level Waste tank that was most recently sampled in late October and early November 1991. Analyses of materials obtained from tank 241-T-111 were conducted to support the Hanford Federal Facility Agreement and Consent Order¹ (Tri-Party Agreement) Milestone M-10-06 (now M-44-05). The waste in tank 241-T-111 is a complex material primarily made up of water and inorganic salts in a gel-like matrix. The insoluble solids are a mixture of phosphates, silicates, oxides, and hydroxides in combination with lanthanum, calcium, manganese, iron, bismuth, uranium, and chromium. The soluble analytes are primarily sodium, nitrate, sulfate, and fluoride (see Table ES-1).

Exotherms over -215 cal/dry gram were detected in the first two segments from each core. As a result of these analyses, tank 241-T-111 has been placed on the Organic Watch List². The source of these exotherms remains under investigation; however, under present tank conditions, there is no possibility that a rapid exothermic reaction will occur. Another finding from the characterization analyses was that the present method for determining or measuring total organic carbon was not effective for the organic materials in this waste matrix. Further investigation of the method failure for this waste is underway and other assay methods are being considered.

¹Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order*, 2 vols. as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

²Wicks, J. H. 1994, *Tank T-111*, (Internal Memo 94-003 to D. A. Turner, March 3) Westinghouse Hanford Company, Richland, Washington.

Comparisons of the calculated bulk inventories for various analytes of concern show that tank 241-T-111 is within established operating safety requirements for heat-load, ferrocyanide, and plutonium inventory. From assessment of past and present surveillance data, tank 241-T-111 is considered an assumed leaking tank (see Table ES-2). Mitigation presently is taking place to remove the remaining free liquid in the tank in order to forestall any further leakage of tank contents to the environment. The free liquid is being transferred to tank 241-SY-102 as part of the overall single-shell tank stabilization effort³.

The results of the analyses have been compared to the dangerous waste codes in the "Washington Dangerous Waste Regulations" (WAC 173-303)⁴. This assessment was conducted by comparing tank analyses against dangerous waste characteristics ("D" waste codes) and against state waste codes. The comparison did not include checking tank analyses against "U," "P," "F," or "K" waste codes because application of these codes is dependent on the source of the waste and not on particular constituent concentrations. The results indicate that the waste in this tank is adequately described in the Dangerous Waste Permit Application for the Single-Shell Tank System; this permit is discussed in the Tank Characterization Reference Guide.⁵

³Jenkins, C. E. and D. B. Engleman, 1994, *Engineering Report: Managing the Assumed Leak from Single-Shell Tank 241-T-111*, WHC-SD-WM-ER-337, Westinghouse Hanford Company, Richland, Washington.

⁴WAC 173-303, "Dangerous Waste Regulations", *Washington Administrative Code*, as amended, Olympia, Washington.

⁵De Lorenzo, D. S., et al. 1994, *Tank Characterization Reference Guide*, WHC-SD-WM-TI-648, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Analysis of the process history of the tank provided valuable information about the likely physical and chemical condition of the waste. Direct comparisons with historical tank reviews underway at Los Alamos National Laboratory are not possible at this time because the Los Alamos National Laboratory effort has not progressed to encompass tank 241-T-111. However, estimates and comparisons using the available process knowledge⁶ have been made. Further comparisons with the Los Alamos National Laboratory database will be made when it becomes available in 1995. The available historical information, in combination with the analysis of the tank waste, supports the conclusion that a rapid exothermic reaction in tank 241-T-111 with the present tank conditions is not plausible because of the high moisture content of the waste and lack of any concentrated heat source. Therefore, the contents of tank 241-T-111 present no credible imminent threat to the workers at the Hanford Site, the public, or the environment. Because an exothermic reaction is not credible, the consequences of this accident scenario, as promulgated by the General Accounting Office, are not applicable.⁷ However, until the source and mechanism of the exotherm is further clarified, it was considered prudent to list the tank on the Organics Watch List, apply more rigorous access controls, and conduct further intrusive operations in tank 241-T-111 with greater care.

⁶Agnew, S. F., 1994, *Hanford Defined Wastes: Chemical and Radionuclide Compositions*, LA-UR-94-2657, Los Alamos National Laboratory, Los Alamos, New Mexico.

⁷Peach, J. D., 1990, *Consequences of Explosion of Hanford's Single-Shell Tank are Understated*, (Letter B-241479 to C. M. Synar, Chairman of Environment, Energy, and Natural Resources Subcommittee, Committee on Government Operations, House of Representatives), GAO/RCED-91-34, General Accounting Office, Washington, D.C.

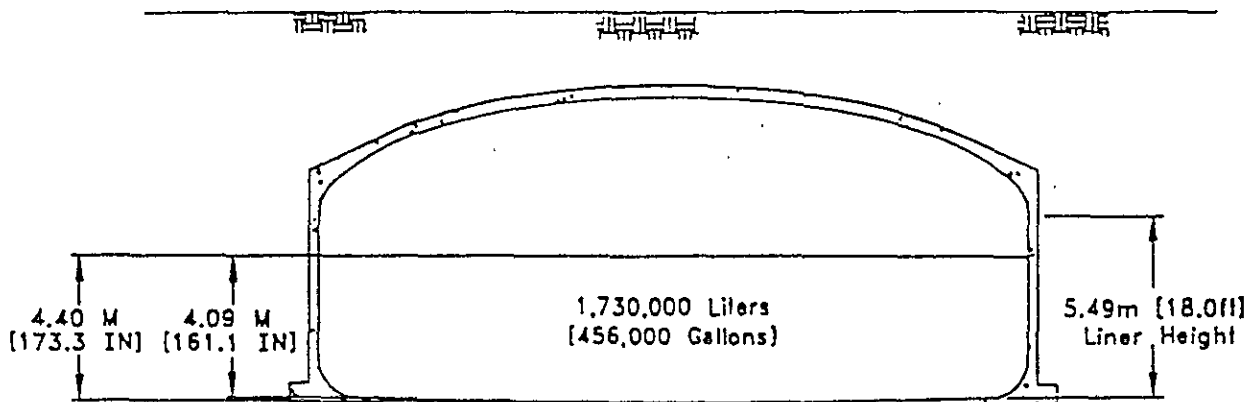
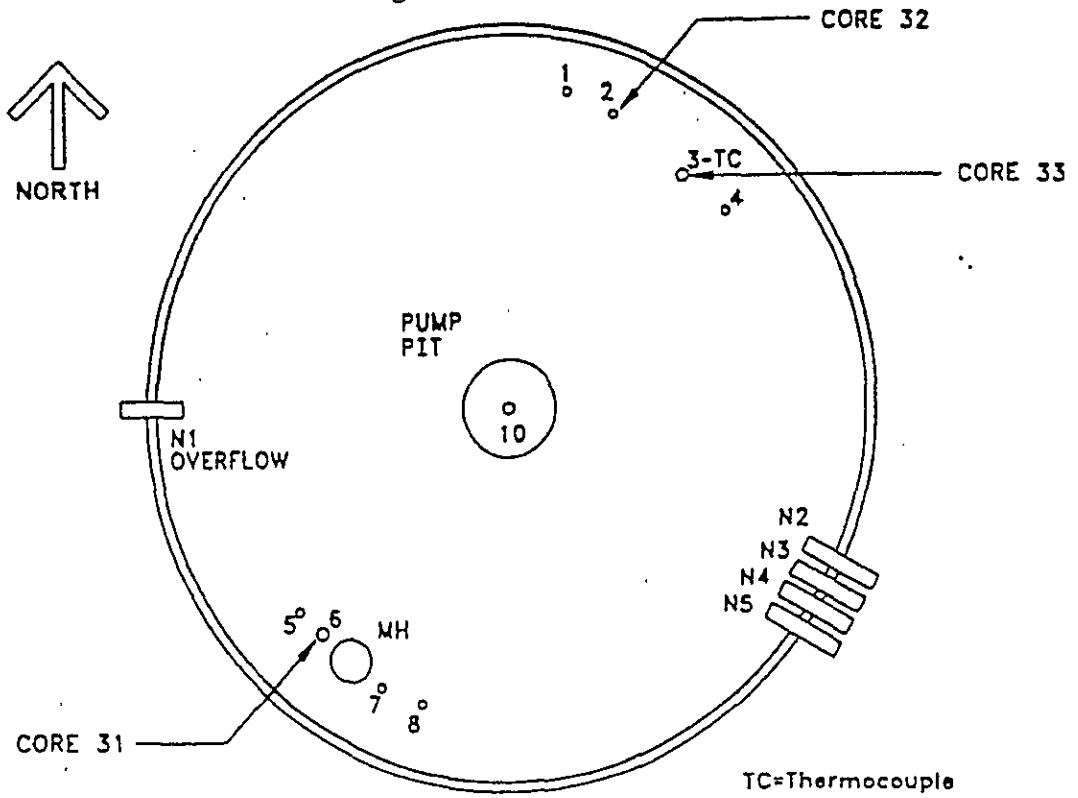
Table ES-1. Single-Shell Tank 241-T-111 Concentrations and Inventories for Critical List Analytes.

Physical Properties		
Density 1.16-1.28 g/mL	H ₂ O 76.0%	1,650,000 kg
Temperature 16 °C	Heat Load 81 w	(24 BTU/hr)
pH 11.65	Total Waste Mass	2,171,000 kg
Chemical Constituents	Average Concentration (wt%)	Bulk Inventory (kg)
Calcium (Ca)	0.242	5,260
Chromium (Cr)	0.198	4,290
Iron (Fe)	1.85	40,200
Manganese (Mn)	0.633	13,700
Sodium (Na)	3.70	80,300
Bismuth (Bi)	2.60	56,300
Lanthanum (La)	0.422	9,200
Silicon (Si)	0.567	12,300
Uranium (U)	0.355	7,700
Total Phosphate (PO ₄ ⁻³)	3.23	70,100
Sulfate (SO ₄ ⁻²)	0.355	7,700
Nitrate (NO ₃ ⁻)	4.13	89,700
Fluoride (F ⁻)	0.230	4,990
Total Organic Carbon (TOC)	0.312	6,770
Radionuclides	(μCi/g)	(Ci)
Total Plutonium	0.304	660
²⁴¹ Am	0.0425	92.4
⁹⁰ Sr	5.41	11,800
¹³⁷ Cs	0.166	360

Table ES-2. Tank 241-T-111.

Tank Description	
Type:	Single-Shell
Constructed:	1944
In Service:	1945
Diameter:	75 ft (22.9 m)
Usable Depth:	17 ft (5.2 m)
Operating Capacity:	530,000 gal (2.01E+06 L)
Bottom Shape:	Dished
Hanford Coordinates:	43.347° North 75.737° West
Ventilation:	Passive
Tank Status: as of May 1994	
Contents:	Non-Complexed Waste
Total Waste:	456,000 gal (1.73E+06 L)
Supernate Volume:	0 gal (0 L)
Drainable Interstitial Liquid:	51,000 gal (193,000 L)
Manual Tape Surface Level (under riser):	161.1 in. (408.9 cm)
Liquid Observation Well Level:	158.8 in. (403.4 cm)
Integrity Category:	Assumed Leaker
Watch List Status:	Organic

Figure ES-1.



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LIST OF ACRONYMS/ABBREVIATIONS

2C	Second-Cycle Decontamination Waste From The Bismuth Phosphate Process
224	Lanthanum Fluoride Waste
AA	Atomic Absorption
ANOVA	Analysis Of Variance
CI	Confidence Interval
DSC	Differential Scanning Calorimetry
EPA	U.S. Environmental Protection Agency
GEA	Gamma Energy Analysis
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
LL	Lower limit
PNNL	Pacific Northwest National Laboratory
RPD	Relative Percent Difference
SST	Single-Shell Tank
TGA	Thermogravimetric Analysis
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
Tri-Party Agreement	<i>Hanford Federal Facility Agreement And Consent Order</i>
TWRS	Tank Waste Remediation System
UL	Upper limit
WHC	Westinghouse Hanford Company

TANK CHARACTERIZATION REPORT: TANK 241-T-111

1.0 INTRODUCTION

In late October and early November of 1991, single-shell tank (SST) 241-T-111 was sampled and analyses were conducted on the materials obtained to complete *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) Milestone M-10-00 (Ecology et al. 1992) to sample and analyze two cores from each tank. Other objectives that these measurements and inventory estimates support are as follows:

- Obtain estimates of both the concentration and total quantity of key analytes relating to safety issues, such as organics and radionuclides.
- Provide input to risk assessment-based disposal decisions for the waste.
- Implement physical property measurements, such as rheology, bulk density, and particle size. These measurements are necessary for the design and fabrication of retrieval, pretreatment, and vitrification systems.

1.1 PURPOSE

The purpose of the tank characterization report is to describe and characterize the waste in SST 241-T-111, based on information from various sources. This report summarizes the available information regarding the waste in tank 241-T-111, and arranges this information in a format useful to support management and technical decisions concerning this waste tank.

1.2 SCOPE

This report presents a broad background of information that was available before core sampling, which initially guided the development of the sampling and analysis program. This material includes process stream data, historical information about any previous characterization testing, transfer records, and observations from in-tank photographs. The results of tank 241-T-111 core-sample analyses are summarized and presented, along with a statistical interpretation of the data. The information obtained from historical sources will be compared and correlated with the actual waste measurements in this report. As characterization efforts proceed and additional information becomes available, this document will be revised periodically to reflect the new data set.

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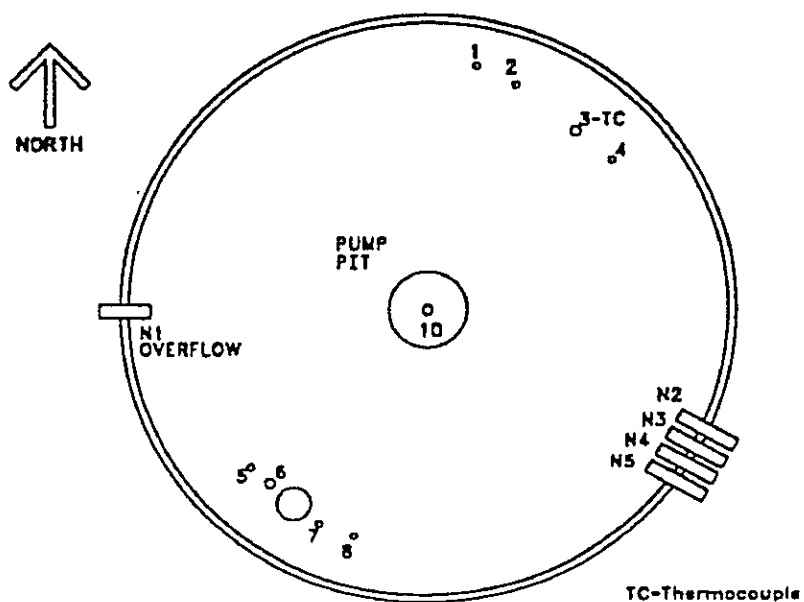
2.0 HISTORICAL TANK INFORMATION AND EVALUATION

2.1 BACKGROUND

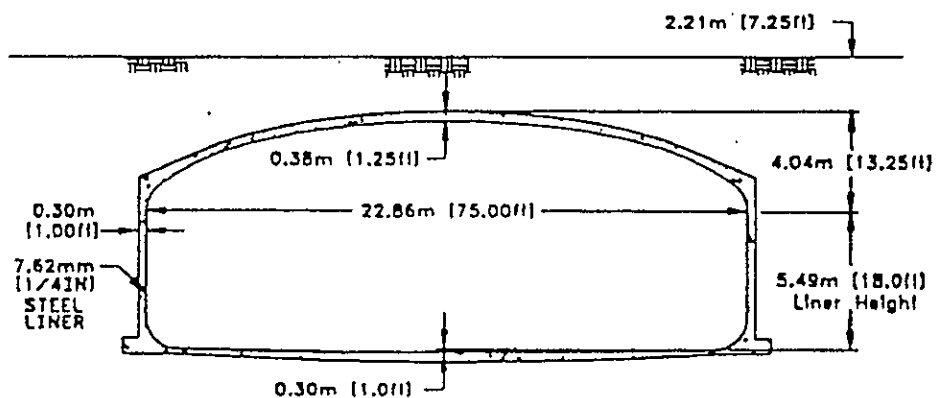
Radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the late 1940s. The original tank farms (B, C, T, and U) were built from 1943 to 1944. Tank 241-T-111 was placed into service in 1945. Groups of waste tanks that were physically located together and built at the same time are called tank farms. Each original tank has a diameter of 22.9 m (75 ft), an operating depth of 5.2 m (17 ft), and a nominal capacity of 2 million liters (530,000 gal). The basic design of a typical SST is shown in Figure 2-1. The tanks were constructed of reinforced concrete with a mild steel liner covering their bottoms and sides. The carbon steel liners were designed to receive and contain neutralized, mildly alkaline wastes. The tops of the tanks are concrete domes. Tanks such as 241-T-111 were all covered by at least 1.8 m (6 ft) of soil for shielding purposes (Anderson 1990). The tanks in the tank farms were connected in groups of three or four and overflowed from one to another in a configuration known as a cascade.

Tank 241-T-111 is the middle tank in a cascade that includes 241-T-110 and 241-T-112. Cascades served several functions in Hanford Site waste management operations. By cascading tanks, fewer connections needed to be made during waste disposal. Consequently, all three tanks were usable without having to connect the active waste transfer line directly to each individual tank. This handling method reduced the likelihood for personnel exposure to the waste and diminished the chances for a loss of tank integrity because of overfilling. Another benefit of the cascades was clarification of the wastes. When used in this manner, most of the solids in the waste slurries routed to the tanks settled in the first tank (241-T-110), and the clarified liquids cascaded on to the other tanks in the series (241-T-111 and 241-T-112). Supernate from the final tank in a cascade series was sometimes routed to a disposal trench. Since most radionuclides are insoluble in aqueous alkaline media, clarification reduced the potential amount of radiological contamination to the environment. However, historical sources report that cascade lines routinely clogged (Anderson 1990). When clogging occurred, very little could be done to resolve the problem, other than rerouting the effluent stream directly to the disposal tank. Cascading was a common practice in the early process history of the tanks, but became less frequent as time passed, virtually ceasing by the late 1950s.

Figure 2-1. Typical Single-Shell Tank Diagram.



TANK RISER LOCATION



Note: Tank 241-T-111 has a dished bottom.

2.2 TANK 241-T-111 HISTORY

The first type of waste that tank 241-T-111 received and stored was second-cycle decontamination waste from the bismuth phosphate process (2C) (1945 to 1952). The tank was filled by a cascade of 2C waste in the fourth quarter of 1945. The supernatant in the tank was disposed to a crib in the third and fourth quarters of 1947. The tank was then re-filled with 2C waste in the second quarter of 1948. After the cascade was filled again in late 1948, tank 241-T-111 remained in active service. From 1953 to 1955, tank 241-T-111 was used to cascade 2C and lanthanum fluoride waste (224) from the LaF_3 finishing process in T Plant to a crib. In addition, Anderson (1990) reports that some 5-6 cell drainage out of B Plant was routed to the tank along with 224 waste in 1952.

After the end of the T Plant cascade in 1955, the reported total waste volume remained relatively unchanged [between 1.98 and 2.12 million L (524,000 and 560,000 gal)] for the remainder of the tank's active service life. There was a residual heel of at least 1.85 million L (488,000 gal) left from previous waste management operations. Tank 241-T-111 remained in 2C service through the third quarter of 1956 (T Plant ran BiPO_4 until August 1956). Anderson (1990) notes that in 1952 the tank was also receiving 224 waste from the plutonium purification/concentration processes performed in the 224-T building.

T Plant initially was built as a bismuth phosphate processing plant, however that purpose was changed when it became an equipment decontamination facility. The tank would have also received miscellaneous decontamination chemicals from T Plant decontamination operations performed in the 1960s. The records are not clear whether tank 241-T-111 always received waste as overflow from tank 241-T-110, or if waste was later routed directly to it. There is anecdotal evidence that the cascade overflow line plugged early in the service life of tank 241-T-110, and that a direct discharge line from T Plant was used to dispose of wastes to tank 241-T-111, however no reference confirming this fact can be found. Between 1964 and 1974, the reported solids volume fluctuated widely between 1.93 and 0.88 million L (510,000 and 233,000 gal). A highly anomalous reading of 150,000 L (40,000 gal) is not considered credible and is believed to be the result of a transcription error. In that time period, the total volume reported rose slightly, then decreased from 2.06 million L to 1.85 million L (541,000 to 488,000 gal) (Anderson 1990). In the second quarter of 1974, there were two small transfers out of Tank 241-T-111: one of 106,000 L (28,000 gal) to tank 241-S-110 and one of 53,000 L (14,000 gal) to tank 241-T-109.

In the third quarter of the same year, dry wells 50-11-05 and 50-11-08 were drilled and in the fourth quarter of 1974, tank 241-T-111 was removed from active service. In the first and second quarters of 1976, two minor transfers of 30,300 L and 19,000 L (8,000 and 5,000 gal), respectively, were made out of tank 241-T-111. Saltwell pumping commenced in the third quarter of 1976 as part of the tank stabilization effort, and no further waste receipts were made. In 1979, the integrity of the tank was questioned and dry well 50-11-11 was drilled in the third quarter. As a result of an observed level drop, tank 241-T-111 was declared an assumed leaker in 1984 (Hanlon 1994). Figure 2-2 illustrates the fill and transfer history of 241-T-111.

The wide fluctuation in the early reported solids level makes it difficult to derive any firm conclusions regarding the stratification in the tank on a strictly historical basis. Overall sludge volume in the tank may have decreased somewhat between 1956 and 1974 with further settling and compaction from the weight of overlying solids. The amount of sludge added since the end of the T Plant cascade activity probably is negligible, because the transfer history of the tank was so limited. Floating suction pumps do not transfer solids readily, and the movement of more than 950,000 L (250,000 gal) of solids in a quarter seems unlikely. However, the reported solids measurement in the fourth quarter of 1956 [1.93 million L (510,000 gal)] and the reported solids measurement at the end of the tank's active service life in 1980 [1.85 million L (488,000 gal)] appears to be reasonable, a 4.5 percent difference, given the time and compaction processes ongoing in the tank, and the inherent uncertainties associated with early solids measurements in the tank farms.

2.3 PROCESS KNOWLEDGE

Process knowledge obtained from historical records can be used to predict the major constituents and some general physical properties of the waste matrix in the tanks. Tank 241-T-111 is expected to contain relatively soft sludge, which can be push-mode sampled. During its operating history, tank 241-T-111 was never subject to any of the various waste volume reduction or in-tank solidification processes. Consequently, there was no formation of hard salt cake on top of the sludge, as there was in the BY or TX Tank Farms (Anderson 1990). This expectation was supported by inspection of in-tank photographs that indicated a moist and pliant waste surface (see Figures 2-3 and 2-4). The effluents that were added to the tank during waste management operations were slurries consisting primarily of water (Schneider 1951). There was no mixing equipment in tank 241-T-111 to blend the layers of settled solids together and there were distinct differences in the composition of wastes directed to it over its operating life. Agnew (1994) predicts that 2C and 224 wastes are not identical in makeup, and analytically observable variations in composition are expected. Because of the lack of agitation or mixing in the tank, observable evidence of layering is expected in some of the segment-level analytical results.

Previous analytical data on tank 241-T-111 is scant. The results of some liquid samples taken in 1974 are provided in Appendix C in WHC-EP-0806 (Simpson 1994). Because the tank has been pumped several times since those samples were taken, they are not considered representative of the present waste matrix. The lower solids in tank 241-B-110 should be similar to the lower solids in tank 241-T-111 (Borsheim 1994). Both tanks were filled at least twice with 2C. Tank 241-B-110 was the first tank in the B Plant 2C cascade while tank 241-T-111 was the second tank in the T Plant 2C cascade. Further studies and comparisons of tank compositions will be forthcoming, pending additional analytical information on the various waste types and matrices that exist in the tank farms. The solids from the neutralized solution would have settled out in the tanks while the supernatant was disposed to cribs. The upper solids of tank 241-T-111 should have some similarity to the B and T 200-series tanks, because they all received 224 waste.

The estimated composition of neutralized 2C and 224 waste streams (i.e., unsettled) are given in Table 2-1 as determined from Schneider (1951). The Schneider (1951) process stream compositions are for the unsettled wastes being transferred from the separations plants. The estimates using Agnew (1994) provide insight to the analyte concentrations of the settled sludge. How the waste settled, the solids content of the settled waste, and how it affected the waste inventory of the tank will be discussed further in Section 6.0.

Table 2-1. Typical Waste Stream Compositions and Expected Sludge Compositions for Selected Analytes (Wet Basis).

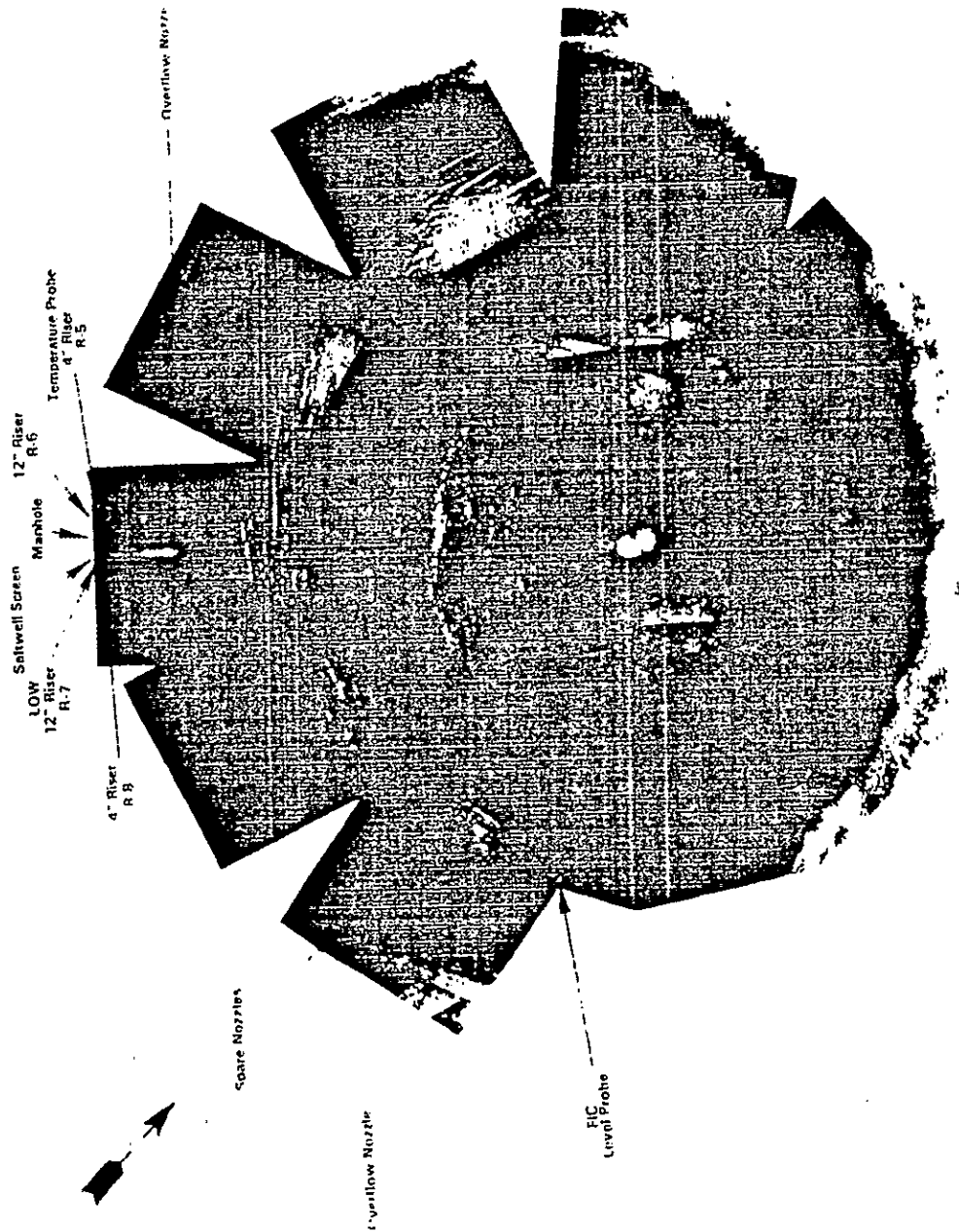
Analyte	Unsettled 2C BiPO ₄ waste (Schneider 1951)		Settled 2C BiPO ₄ waste, (Agnew 1994) average 1944-1951 and 1951-1956 compositions		Unsettled BiPO ₄ -LaF ₃ 224 process waste (Schneider 1951)		Settled BiPO ₄ -LaF ₃ 224 process waste (Agnew 1994)	
	Wt %	(μg/g)	Wt %	(μg/g)	Wt %	(μg/g)	Wt %	(μg/g)
Bi	0.12	1,200	2.55	25,500	0.11	1,100	2.07	20,690
Cr	0.006	60	0.0033	33	0.016	160	0.0035	35
Na*	3.5	35,000	6.46	64,600	3.39	33,900	8.50	85,000
NH ₄ ***	0.16	1,600	-	-	0.011	110	-	-
Fe	0.17	1,700	1.79	17,900	-	-	0	0
Mn	-	-	0	0	0.031	310	0.019	190
K	-	-	0	0	0.79	7,900	0.779	7,790
La	-	-	0	0	0.05	500	2.67	26,700
Anions								
PO ₄ ³⁻	2.2	22,000	5.63	56,300	0.28	2,800	1.25	12,500
SO ₄ ²⁻	0.34	3,400	0.276	2,760	0.032	320	0	0
NO ₃ ⁻	5.8	58,000	4.28	42,800	3.91	39,100	6.16	61,600
F ⁻	-	-	0.494	4,940	0.52	5,200	4.66	46,600
SiF ₆ ²⁻	0.35	3,500	-	-	-	-	-	-
C ₂ O ₄ ²⁻	-	-	-	0	0.12	1,200	1.52	15,200
H ₂ O	87.3	873,000	76.0	760,000	90.75	907,500	69.0	689,600

*Analytes listed in *italics* are mostly soluble.

**NH₄⁺ probably has dissipated over time and is believed to be no longer present.

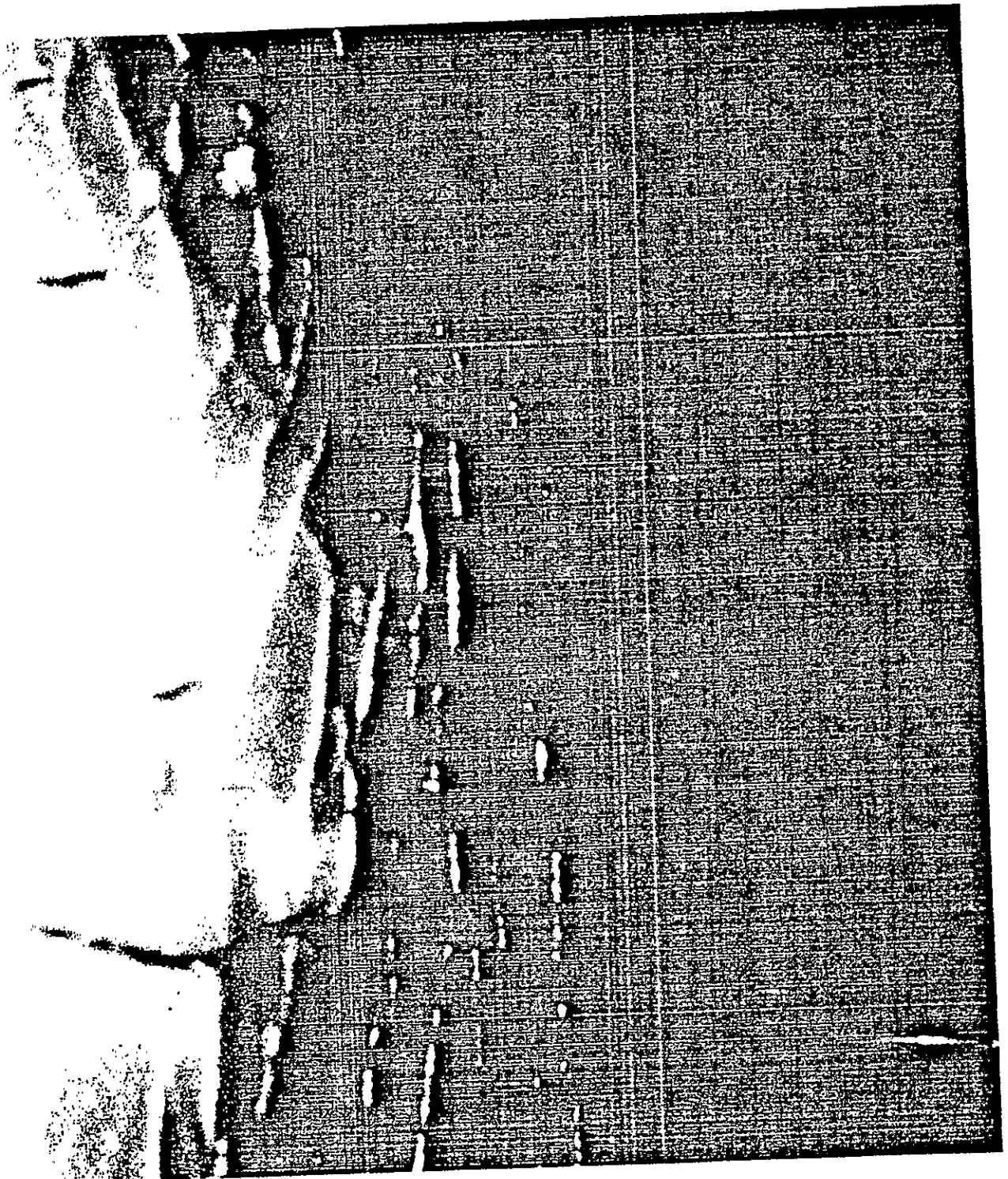
Figure 2-3. 241-T-111 Surveillance Photo - Collage.

241-T-111
 11/10/99 12:00



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Figure 2-4. 241-T-111 Surveillance Photo - Close up.



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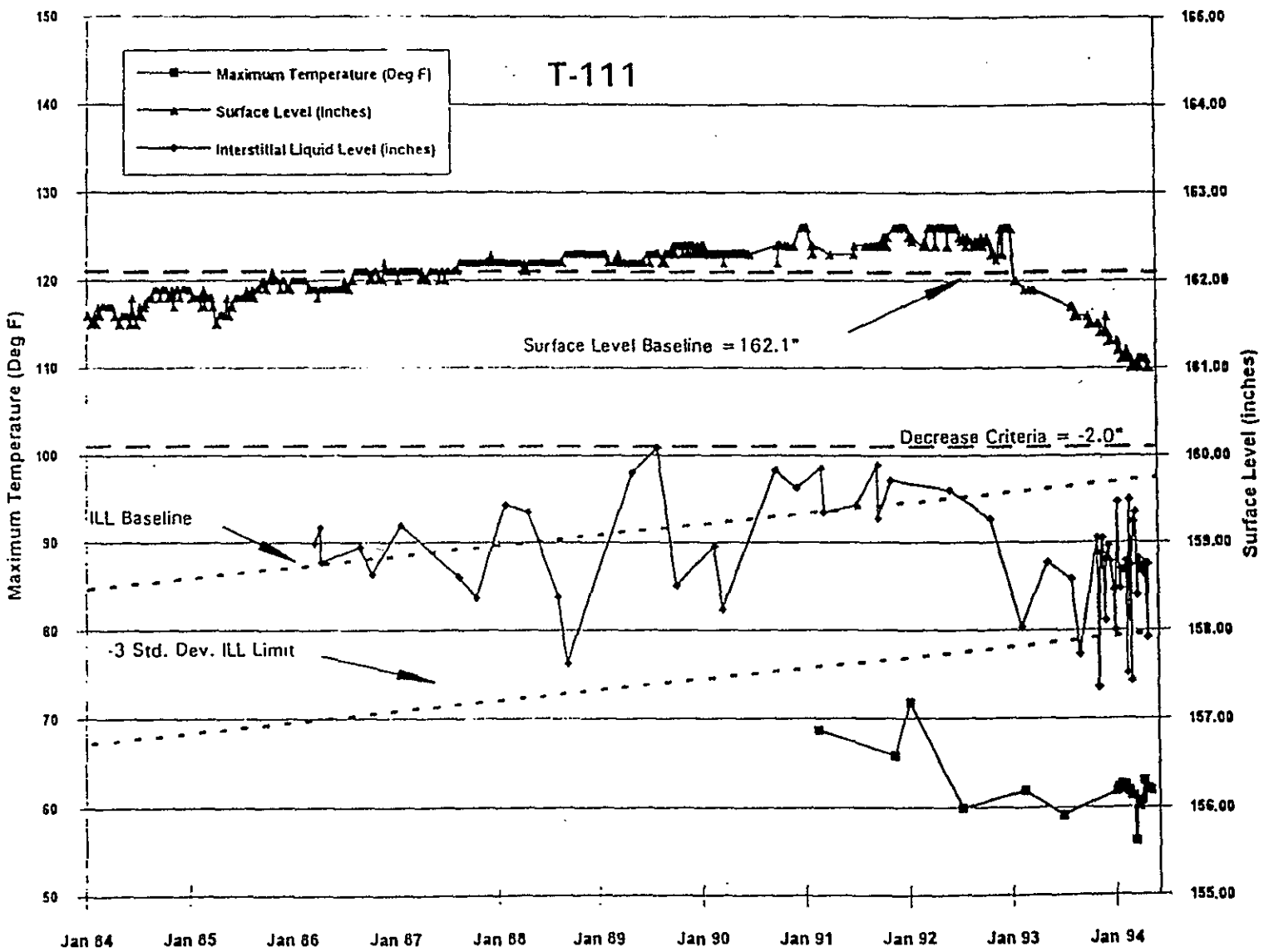
2.4 SURVEILLANCE DATA

The most recent waste inventory measurement for tank 241-T-111 reports approximately 1.73 million L (456,000 gal) of solid waste with an estimated 193,000 L (51,000 gal) of drainable liquids (Hanlon 1994). The most recent surveillance data shows a discernable downward trend over the past 18 months, nearly a 3.8 cm drop in surface level, after a very long, gradual, but minor upward trend over the last 10 years (see Figure 2-5). This recent behavior possibly indicates further settling, or leaking has taken place. These figures translate to a waste depth of 408.9 cm (161.1 in.) underneath the riser and 440.2 cm (173.3 in.) at the tank centerline. The tank has not been fully interim stabilized yet, and is an assumed leaker. The recent waste temperature in tank 241-T-111, taken from a thermocouple tree is approximately 16 °C (60.5 °F) (Rios 1994), and the estimated heat load in the tank is less than 2.93 kW (10,000 Btu/hr).

2.5 TANK STATUS

Tank 241-T-111 was a non-watch list SST, with no historical indication of any potential safety issue. However, during the review of the energetics data that was done in support of characterization, exotherms in excess of -125 cal/dry gram of waste were noticed in the top 3 segments of core 31 and the top 2 segments of core 33. Additional follow-up work has been done confirming the initial observation and as a result, 241-T-111 has been added to the Organic Tank Watch List (Wicks 1994). The exotherms were not predicted from the process history of the tank and the known characteristics of the 2C and 224 waste streams disposed there.

Figure 2-5. 241-T-111 Surveillance Data.



3.0 TANK SAMPLING OVERVIEW

3.1 DESCRIPTION OF SAMPLING EVENT

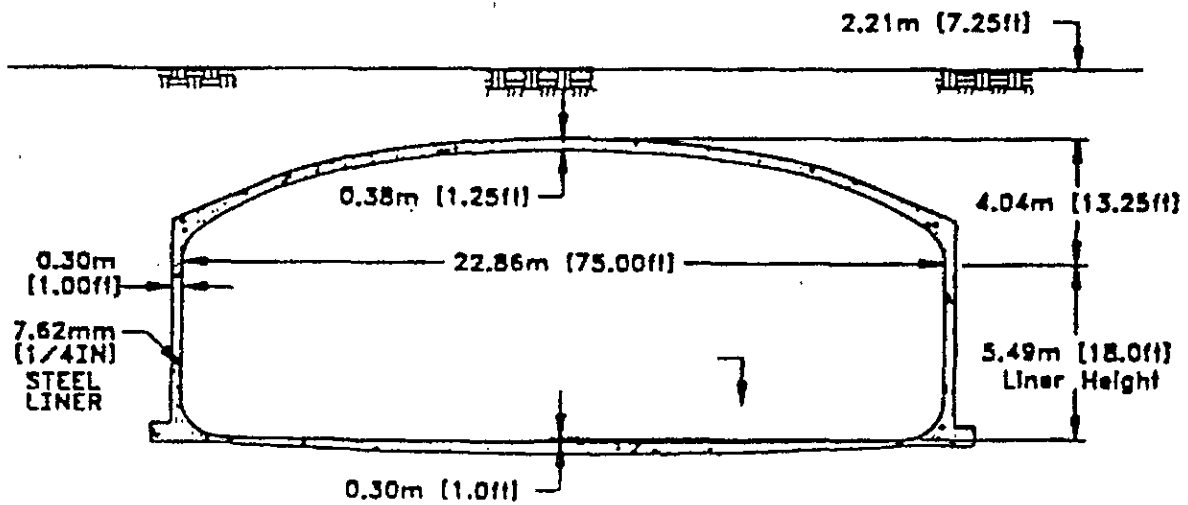
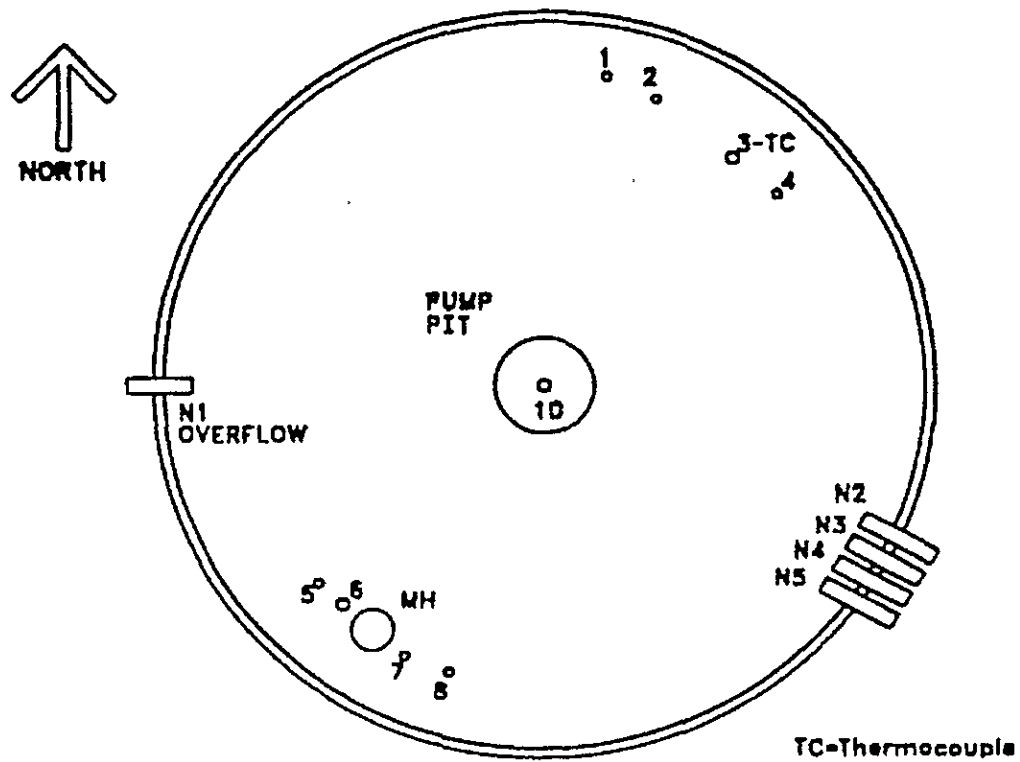
Tank 241-T-111 was push-mode core sampled through three risers during a period from October 22, 1991 to November 7, 1991. The core samples were obtained using a specially designed core sampling truck. Access to the interior of the tank is provided by various tank risers. Risers are pipes of various diameters leading into the tank dome from the ground. The riser configuration for tank 241-T-111 is given in Figure 3-1. A review of the tank farm operating records and a field inspection of the tank risers determine which risers can be used in the sampling operation. During sampling, a riser is opened and the truck is positioned over the riser. The sampler is lowered into the tank through the drill string and pushed into the waste. Further information regarding the core sampling operation can be found in *Tank Farm Operating Procedure* (Ross 1993). Nine segments were expected from each core sample. Each segment is approximately 48 cm (19 in.) long. Core 31 was obtained from riser 6 on October 22, 1991. Core 32 was obtained from riser 2 from October 24, 1991 to October 25, 1991. Core 33 was obtained from riser 3 on November 5, 1991 to November 7, 1991.

The sampler is constructed of stainless steel and is 48 cm (19 in.) long, with a 2.2-cm (7/8-in.) inside diameter, and has a volume of 187 mL (0.05 gal). A hydrostatic fluid of normal paraffin hydrocarbons, similar to kerosene, was used in establishing a head balance while taking these cores. Objections involving sample degradation and contamination have been raised regarding the use of this fluid, and the practice has since been discontinued. However, for cores 31 and 33, nearly full recovery was achieved in every case. There were little or no drainable liquids observed in the sample liners or in the samplers upon extrusion of the samples, and although hydraulic permeability measurements were not taken as part of the characterization effort, the waste did not appear porous. Thus, sample contamination from the hydrostatic fluid is not deemed to be a significant issue with the analysis of the sample or the interpretation of the results.

The casks were transported to the 222-S Laboratory for characterization analysis. This facility is operated by Westinghouse Hanford Company (WHC) in the 200 West Area of the Hanford Site. Further physical and radiochemical characterization was performed at the 325 Laboratory. Specific analyses aimed at identifying and resolving the unusual energetics observed (Bean 1994) are also being done at 325 Laboratory. That facility is operated by Battelle Pacific Northwest National Laboratory (PNNL), and is located in the 300 Area of the Hanford Site.

Before the most recent stabilization effort, a series of liquid grab samples were taken and analyzed to ensure waste compatibility with the tank receiving the 241-T-111 liquid waste. These grab samples were acquired using a sampling method known as "bottle-on-a-string," in which a weighted bottle with a shuttered mouth is lowered into the liquid waste. The bottle's mouth is opened, it fills with liquid, the mouth is closed, and the sample is retrieved and transported to the 222-S Laboratory. Winters et al. (1990a and 1990b) has a more detailed description of this sample method.

Figure 3-1. Tank 241-T-111 Riser Configuration.



3.2 CHAIN-OF-CUSTODY

A chain-of-custody record was kept during the sampling event for each segment that was sampled. The chain-of-custody form is a one-page record that is used to ensure that (1) the sample is safely and properly transported from the field to the laboratory, and (2) the correct personnel are involved in the sampling operation and transportation of the sample to the laboratory.

One of the additional functions of the chain-of-custody record is to provide radiation survey data. This is a record of the radiation dose that is emitted from the shipping cask. The dose rates in mrem/hour are measured from the top, sides, and bottom of the cask. These values are recorded on the chain-of-custody record and represent the radiation being emitted directly from the sample. The last item recorded under the radiation survey data is the smearable contamination. Smearable contamination represents the radiation from waste material that is not sealed within the shipping cask; values greater than 100 mrem/hour are considered unsafe. Measurements are made both in the field and in the laboratory. No smearable contamination was found with these samples.

The chain-of-custody has several other important functions: (1) to provide a modest description of the cask, sampler, and the expected contents of the sampler (shipment, sample, and cask serial numbers for the specific sampling event); (2) to provide summary information about the analytical suite that the sample will undergo or reference the salient documentation; (3) to provide traceability for the sample during transport; and (4) to ensure sample integrity on arrival at the laboratory. This information is provided to ensure that each sample can be uniquely identified. A summary of the most pertinent data contained in the chain-of-custody forms for the tank 241-T-111 samples is presented in Tables 3-1 and 3-2.

Copies of the chain-of-custody forms are available in the full data package and through Hanford Site Central Files. From inspection of the chain-of-custody records, there appear to be irregularities in the sampling and transport of tank 241-T-111 samples. Valve failures were observed in individual segments in all three core samples, and core 32 was considered to be completely compromised and non-representative. Each segment was almost entirely aqueous, containing at most a small amount of suspended solids. Liquid was also found in some of the liners surrounding the samplers from core 32, and was assumed to be leakage from the sampler. These irregularities merit a sampling concern, sample integrity concern, and potential safety concern (i.e., sample containment was compromised). However, the double-containment strategy employed in the handling of the samples was successful in preventing any excessive radiological exposure to personnel and no material escaped confinement. Further investigation and refinement of the sampling process, procedures, and sampler design is in progress.

Table 3-1. Core 31 - Chain-of-Custody Summary.

Sample	Core 31	
Place Taken	241-T-111 Riser 6	
Date Taken	10/22/91	
Date Released	10/23/91	
Time Released	9:35 P.M.	
Sender	D. C. Hartley	
Receiver	V. Johansen	
Place Received	222-S Laboratory	
Time Received	10:00 P.M.	
Sample Number	Smearable Contamination	Dose Rate Through the Drill String
91-090 (Segment 1)	< DL alpha < DL beta-gamma	4.5 mR/hr
91-091 (Segment 2)	< DL alpha < DL beta-gamma	2.4 mR/hr
91-092 (Segment 3)	< DL alpha < DL beta-gamma	2.5 mR/hr
91-093 (Segment 4)	< DL alpha < DL beta-gamma	2.0 mR/hr
91-094 (Segment 5)	< DL alpha < DL beta-gamma	1.5 mR/hr
91-095 (Segment 6)	< DL alpha < DL beta-gamma	1.5 mR/hr
91-096 (Segment 7)	< DL alpha < DL beta-gamma	0.5 mR/hr
91-097 (Segment 8)	< DL alpha < DL beta-gamma	1.5 mR/hr
91-098 (Segment 9)	< DL alpha < DL beta-gamma	0.3 mR/hr

< DL = below detection limit.

Table 3-2. Core 33 - Chain-of-Custody Summary

Sample	Core 33		
Place Taken	241-T-111 Riser 3		
Dates Taken	11/5/91 to 11/6/91		
Dates Released	11/6/91 to 11/7/91		
Sender	D. C. Hartley		
Receiver	V. Johansen		
Place Received	222-S Laboratory		
Times Received	See Below		
Sample Number/ Date Sampled	Date Released/ Time Released/ Time Received	Smearable Contamination	Dose Rate Through the Drill String
91-108 (Segment 1) 11/5/91	11/6/91 10:10 10:55	< DL alpha < DL beta-gamma	3 mR/hr
91-109 (Segment 2) 11/5/91	11/6/91 10:10 10:55	< DL alpha < DL beta-gamma	2.5 mR/hr
91-110 (Segment 3) 11/5/91	11/6/91 10:10 10:55	< DL alpha < DL beta-gamma	10 mR/hr
91-111 (Segment 4) 11/5/91	11/6/91 14:10 14:30	< DL alpha < DL beta-gamma	5 mR/hr
91-112 (Segment 5) 11/6/91	11/6/91 14:10 14:30	< DL alpha < DL beta-gamma	< 0.5 mR/hr
91-113 (Segment 6) 11/6/91	11/6/91 14:10 14:30	< DL alpha < DL beta-gamma	2 mR/hr
91-114 (Segment 7) 11/6/91	11/7/91 10:10 10:35	< DL alpha < DL beta-gamma	1.5 mR/hr
91-115 (Segment 8) 11/6/91	11/7/91 10:10 10:35	< DL alpha < DL beta-gamma	1 mR/hr
91-116 (Segment 9) 11/6/91	11/7/91 10:10 10:35	< DL alpha < DL beta-gamma	1 mR/hr

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4.0 SAMPLE HANDLING AND ANALYTICAL SCHEME

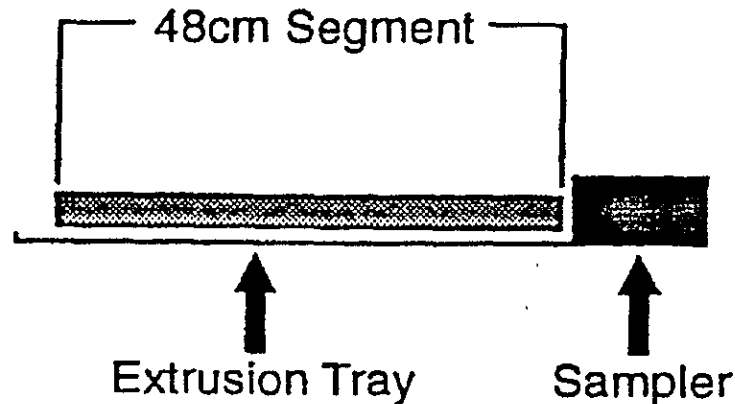
The primary objective for these waste analyses was to meet requirements of the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Ecology et al. 1992, Ecology et al. 1994). Two composites from each core were built and analyzed in accordance with the complete baseline case core composite scenario detailed in WHC-EP-0210 (Winters et al. 1990a, Winters et al. 1990b) and as amended by Hill et al. (1991). However, there are other concerns and interests for this data. First, this information will help to evaluate whether constituent concentrations are within safe operating limits by determining whether they are flammable or explosive. Second, analyte concentrations of interest to the various Hanford Site technical programs can be determined.

Because tank 241-T-111 initially was identified as a non-watch-list tank, extensive analytical measurements were not specified to resolve any previously identified safety concerns associated with this tank. The analysis horizon for characterization was determined to be on the core composite level with selected analyses being performed on a segment-level basis. However, after the discovery of substantial exotherms in the top 100 cm (40 in.) of the waste, additional testing on a segment level basis was done on those samples exhibiting reactive behavior. This additional testing, with an emphasis on providing resolution to the safety issues raised by the presence of the exotherms in the waste is still underway at the time of the writing of this report. This report will be updated to reflect the new data or root causes of the energetics when that information becomes available.

4.1 SAMPLE BREAKDOWN PROCEDURE

In order to obtain the sample, the sampler is shipped in a vertical position and removed from the shipping cask directly into the hot cell. At this time, the sampler must be placed in the horizontal position. The sample is then loaded into the mechanical extruder and removed by pushing it out from the back of the sampler with a piston. In this case, the sampler is pressed against a fixed piston, forcing the sample into the extrusion tray. If a full sample is captured, the material nearest the valve will be from a deeper part of the tank. The material near the piston is closer to the surface. The sample and any liquids are collected on a metal tray. Next, the mass of the segment and the approximate length are recorded. From this information, the gross bulk densities of the segments can be estimated until further physical properties work is performed. The sample volume is determined by measuring the length of the extruded sample using a linear unit volume of 9.85 mL/in. Figure 4-1 illustrates how the SST segment sample was extruded. Color photographs documenting the extrusions of each of the segments from tank 241-T-111 were taken and are on file at the 222-S Laboratory.

Figure 4-1. Typical Single-Shell Tank Segment Extrusion.



Several different styles of nomenclature presently are used for distinguishing core samples, sample segments, and subsegments in the existing literature. Two major conventions are used in the documentation relating to core sampling in general. The first is designating the segment with the last two digits of the calendar year (92-) and then numbering the segments sequentially (-001, -002, etc.). This system resets itself every calendar year. The second system distinguishes the tank, core, segment (and subsegment, if necessary), with segment 1 being the at the top of the core sample and having the number increase as a function of depth in the tank so that segment 9 is at the bottom of the tank in 241-T-111. An example of this naming protocol for the second segment of the first core is 241-T-111-Core 31-Segment 2. Where no tank identification is given in this report, it is understood to mean tank 241-T-111.

4.2 TANK 241-T-111 CORE SAMPLE DESCRIPTION

The location of the risers, the dished bottom of the tank, and safety margins in the sampling protocol preclude obtaining samples from the entire waste depth in the tank. In addition, the sampling protocol establishes that segments will be calculated from the bottom up. Thus, depending on the waste depth, maximum recovery for the top segment from tank 241-T-111 is not necessarily going to be a full 48-cm (19-in.) segment. However, for cores 31 and 33, sample recovery was excellent; overall recoveries were in excess of 80 percent. Segment recoveries were based on the maximum recoverable volume for the segment regardless of solid/liquid ratio. The core recoveries reported in the data package are determined based on a visual inspection of the sample length and apparent volume at the time the samples are extruded. Further study of the color photographs taken after extrusion can aid in clarifying a rough sample volume. Tables 4-1 and 4-2 present the initial measurements and observations regarding the core samples on extrusion, and an estimated range of the core recovery on a volume basis for cores 31 and 33.

Table 4-1. Tank 241-T-111 Core 31 Sample Description Summary.

Core number (Riser 6)	Segment	Core recovery (Vol. basis)	Total mass (g)	Comments
31	1	27%	64.0	Sampler was nearly empty; contained approximately 50 mL of black/brown low viscosity solids. Apparently homogeneous.
31	2	80-100%	182.8	Sampler was almost completely filled with solids. Again, the material is dark brown or black with a fluid or gel-like consistency, and appears to be homogeneous. A small amount of liner liquid was observed. The liquid was observed to be two phase (NPH and aqueous phases).
31	3	95-100%	162.2	Sampler was almost completely filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous.
31	4	80-100%	153.5	Sampler was almost completely filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous. The top eighth contained waste material that appeared to be more fluid than the rest of the sample. No sampler liquid or liner liquid was observed.
31	5	100%	190.9	Similar to previous observations; no sampler or liner liquid.
31	6	0%	NA	Sampler empty.
31	7	90-100%	186.4	Sampler was almost completely filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous.
31	8	100%	186.4	Similar to previous observations; no sampler or liner liquid.
31	9	100%	203.1	Sample was not homogeneous. Sample began as before (dark brown and viscous), but gradually became lighter as a function of depth. Sample was divided into two portions, a light end (133.4 g) and a dark end (69.7 g). Consistency of the sample remained the same throughout.

Table 4-2. Tank 241-T-111 Core 33 Sample Description Summary.

Core number (Riser 3)	Segment	Core recovery (Vol. basis)	Total mass (g)	Comments
33	1	100%	159.16	Sampler was full of black/brown low viscosity solids. Apparently homogeneous, with no drainable liquid.
33	2	100%	207.59	Sampler was completely filled with solids. Again, the material is dark brown or black with a viscous consistency, and appears to be homogeneous.
33	3	87-100%	167.9	Sampler was nearly filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous.
33	4	75-85%	182.05	Sampler was 75-85% filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous. The valve was observed to be open prior to extrusion. No sampler liquid or liner liquid was observed.
33	5	88%	174.3	Similar to previous observation, the valve was observed open, the sampler had approximately 88% solids, and no drainable or liner liquid was seen.
33	6	100%	217.37	Sampler was almost completely filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous.
33	7	100%	196.91	Sampler was almost completely filled with solids. The waste is dark brown with a thick, viscous consistency, and appears to be completely homogeneous.
33	8	100%	199.8	Similar to previous observations. No sampler or liner liquid.
33	9	100%	191.01	Sample was not homogeneous. Sample began as before (dark brown and viscous) but gradually became lighter in color as a function of depth, similar to core 31. Aliquots from the light and dark portions were taken for VOA and energetics analyses. Consistency of the sample remained the same throughout.

Although samples for core 32 were taken from riser 2, the materials obtained at all levels appeared to be particulate suspended in an aqueous solution, with slight traces of normal paraffin-hydrocarbon contamination observed in a few samples. These samples did not correspond to the observed conditions in the tank and were considered non-representative. The results of the core 32 sampling exercise were attributed to sampler failure, and because no acceptable samples were acquired, no assays were performed. Therefore, no results for core 32 will be reported. Valve failures were reported routinely for all three core samples at deeper positions in the tank. The full data package (McKinney et al. 1993) containing all of the assay results is available from the Hanford Site Central Files.

General characteristics of tank 241-T-111 waste materials are as follows:

- Very little drainable liquid was associated with these samples either in the liner or in the extruder.
- Core samples generally were dark brown or black in color. The brown solids were streaked through with grey/white material.
- The samples had a viscous or gel-like consistency. They were thick, relatively smooth sludges (swamp mud was the descriptive term used by the hot-cell observer). The core materials all appeared to be saturated with liquid, which did not drain.

4.3 HOLD TIME CONSIDERATIONS

All analytes have a predetermined maximum allowable holding time set by the U.S. Environmental Protection Agency (EPA) 1986, during which the analysis should be completed. Completion of analysis during the maximum allowable holding time enhances the regulatory defensibility of the data. The length of the holding time varies for each analyte. For example, analyses performed on volatile and semivolatile organic compounds, many of which decompose or dissipate quickly, have shorter holding times. On the other hand, persistent analytes such as metals (except mercury), do not readily decompose or dissipate, and therefore have much longer acceptable holding times. Nearly all of the analyses of cores 31 and 33 exceeded their respective maximum allowable holding times. The only analyses that came close to meeting holding-time criteria were radiochemistry and metal analyses. Both of these analyses were completed about six months after sampling, and six months is the maximum hold time for these analyses. Although exceeding the maximum allowable holding times weakens the defensibility of the analytical results for some uses, it is anticipated that the overall effect on the analytical results for tank 241-T-111 waste relative to waste management and disposal information needs is minimal. Further discussion of holding times can be found in Winters et al. (1990a).

4.4 SAMPLE PREPARATION

Sample preparation procedures are conducted in order to optimize the recovery of each analyte of interest from the tank waste. Water digestion, acid digestion, and potassium hydroxide fusion commonly are used to extract metals and several radioisotopes from solid samples, and in some cases digestions are performed on liquid samples to improve analytical resolution. Many separations are specific to a particular analysis and are described within the corresponding analytical methods referenced in Section 4.5. In order to verify analyte recoveries resulting from separation techniques, laboratory control samples, carriers, spikes, tracers, and surrogates are analyzed concurrently with the characterization samples.

In some cases no sample preparation is necessary or desired. Direct analyses are assays performed on the sample matrix with little or no sample preparation. Several direct analyses were performed relating to the physical or energetic properties of the waste: density, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gravimetric weight percent water.

Water leach (or water digestion) analyses are assays performed after the sample matrix has been digested in distilled/deionized water. The water is then analyzed for soluble analytes. The soluble anions are determined by ion chromatography (IC). The primary anions analyzed in this manner are fluoride, chloride, nitrate, nitrite, phosphate, and sulfate. In addition, free cyanide and pH were also analyzed from water digestion samples. Note that IC assays use a 1 to 100 sample to water digestion, where pH measurements use a 1 to 1 sample to water ratio. Selected radionuclides were measured on some of the water digestion samples to determine the type and number of water soluble radionuclides. Inductively coupled plasma (ICP) atomic emission spectroscopy and atomic absorption (AA) spectroscopy were also performed on some of the water digestion samples. These assays were performed to determine the amount of soluble metal cations (ICP) or arsenic, mercury, or selenium (AA). In many cases, these analytes were below the detection limits in the water digestion samples, suggesting that most of the analytes are not water soluble.

Acid digestion is a preparation method in which the sample is dissolved in a mixture of nitric and hydrochloric acids. This preparation brings most of the insoluble metals into a solution with a minimum amount of dilution, and usually is best for the detection of trace and some major metals. These properties are the reason that acid digestion generally is used as the sample preparation for the homogenization tests in SW-846-based environmental sampling. However, experience with Hanford Site tank-waste matrices has shown that acid digestion does not always provide complete solubilization, and that a more rigorous dissolution preparation, such as fusion, may be necessary to get adequate quantitation. The analyses performed on this preparation were the ICP, gamma energy analysis (GEA), and AA analysis (the AA analysis used nitric acid only). IC analysis was not performed with the acid digestion preparation solution because that method introduces additional Cl^- or NO_3^- anions, confounding the results for that sample.

Analyses that were performed on fusion-prepared samples were ICP and GEA for radionuclides. Fusion dissolution analyses are assays performed on the sample matrix after it has been fused with potassium hydroxide in a nickel crucible and dissolved in acid. This

preparation dissolves the entire sample, whereas other sample preparation procedures may not completely dissolve the sample matrix. However, one significant disadvantage of fusion preparation is that large amounts of potassium hydroxide are required to bring a sample into solution. Because of this high dilution factor, trace elements are less likely to be quantified correctly, if they are detected at all. Another limitation of the preparation method is if the sample contains substantial quantities of potassium or nickel, these analytes will not be quantifiable because the procedure uses potassium hydroxide and a nickel crucible. This limitation can be overcome using alternate preparation methods if potassium or nickel are analytes critical to interpretation of the data. Elements that occur in abundance, such as major metals, or that are highly insoluble are likely to be detected better by the fusion results than by any other sample preparation.

Generally, fusion dissolution is the preferred method of analyzing radionuclide content, with the exception of ^{14}C , ^{129}I , and ^3H (tritium). However, the sample preparation specified in the test instructions for ^{14}C (water digestion) probably is not best for the high-level waste matrices. Difficulty with dissolving the sample with a water leach, and volatility associated with a fusion preparation, potentially will bias the ^{14}C results low for both sample preparation types if they are associated with the water insoluble solid materials, and similar difficulties are encountered for the other radionuclides mentioned. However, none of these analytes are expected to be significant contributors to the radionuclide content of the waste.

Major metal components that were detected well with fusion ICP analysis for tank 241-T-111 were calcium, chromium, iron, manganese, sodium, bismuth, and lanthanum. Phosphorous, sulfur, and silicon are non-metallic analytes detected by ICP. In the case of these elements, the fusion result is the preferred method of analysis because it is believed to provide more complete dissolution of the waste, and therefore, more complete quantitation of the analytes. Comparisons of these results with the IC results can provide insight to the solubility characteristics of the waste. Some of the primary radionuclides that are measured using this sample preparation are ^{237}Np , $^{239/240}\text{Pu}$, ^{90}Sr , ^{137}Cs , and ^{99}Tc . A total alpha and total beta count were performed on the fusion dissolution samples as well.

As previously noted, chemical and radiological analyses were done largely on core composites, and in these previous characterization efforts, the core composites were built using quantities of segments based on a proportion of the total weight of sample for the core (Winters et al. 1990a, Winters et al. 1990b). This method assumed that the sample obtained is representative of what is in the tank. However, when partially filled segments are obtained, this procedure assumes that the tank does not contain any waste in this area. Incomplete recovery for a segment probably is the result of sampling problems rather than voids in the waste. The approach used in this analysis effort was to composite equal quantities of the homogenized segment material and assume that whatever is obtained in a partial segment is representative of a whole segment. Some inaccuracies may be introduced from this method because of density differences between segments. However, the inaccuracies introduced from density differences probably are small. In general, those deviations are minimal compared to the other errors inherent in core sampling and analysis. If full segments are obtained for the entire core, and the homogenization procedure is satisfactory, there will be little difference between the two approaches.

4.5 ANALYTICAL METHODS

This section briefly describes the analyses used to characterize the waste in tank 241-T-111. The analyses were split between the WHC 222-S Laboratory and PNNL. Several of the analytical tests performed on the composites were also performed on the segments, but on a much more limited scope. There were no free liquids from cores 31 and 33, thus there are no separate liquid core composite results. However, in March 1994, a series of liquid grab samples were taken and analyzed for compatibility considerations (Carothers et al. 1994) before the start of stabilization. These results will be presented with the water digestion results and comparisons and conclusions will be made.

4.5.1 Physical and Rheological Tests

Physical tests completed at the 222-S Laboratory included particle size analysis, TGA, DSC, specific gravity, and percent water analyses. Duplicates were performed for the percent water analyses. The physical properties measured at PNNL included weight percent solids, settling behavior, and weight percent dissolved solids. Rheological testing on these samples were performed at PNNL and included shear strength and shear stress as a function of shear rate. Rheological properties were measured in duplicate. Table 4-3 lists the analytical methods used for physical and rheological testing. Three segments from core 31 (segments 2, 4, and 8) were selected to perform the full suite of rheological and physical measurements, in addition to the particle size assay done on each segment. Viscosity, settling properties, fluid behavior, and shear strength were some of the primary characteristics investigated. The samples tested for these properties were not homogenized before analysis.

Table 4-3. Analytical Methods for Physical and Rheological Testing.

Analyte	Procedure
Particle size	T044-A-01712F
Thermogravimetric analysis	LA-560-112
Differential scanning calorimetry	LA-514-113
Specific gravity	LA-510-112
Percent water	LA-564-101
Rheology	PNL-ALO-501; PNL-ALO-502
Physical properties	N/A

Scanning TGA and DSC are useful in determining the thermal stability or reactivity of a material. TGA measures the mass of a sample while the temperature of the sample is increased at a constant rate. In DSC analysis, the heat absorbed/evolved over and above the usual heat capacity of the substance is measured while the substance is exposed to a linear

increase in temperature. The gravimetric weight percent water was determined by drying the sample for 12 to 24 hours in an oven at 103 to 105 °C and measuring the difference in the weight of the sample.

4.5.2 Chemical and Radionuclide Constituent Analysis

Most of the chemical and radionuclide analyses were performed at the 222-S Laboratory. The uranium and plutonium isotopic analyses, however, were performed at PNNL. Duplicate analyses were performed on every tank sample. Table 4-4 lists the analytical methods used (Winters et al. 1990a, Winters et al. 1990b).

Sample Homogenization

The segment and core composite samples were homogenized using a mechanical mixer before analysis. This was done so that aliquots removed for analysis would be representative of the entire segment or core composite. Aliquots of the homogenized tank waste from core 33, segments 1, 3, 5, 7, and 9, were taken to determine the efficacy of the homogenization procedure. The samples were split into duplicates, acid digested, and assayed by ICP and GEA. This procedure is done to determine if the degree of mixing achieved by the as-planned homogenization procedure was sufficient to achieve sample homogeneity. Since the homogenization samples are evaluated concurrently or after the other core samples, the results provide only an estimate of subsampling error (or variation). They were not used in this case to ensure that homogenization was achieved before analysis. However, after review of the results, it appears that homogenization of the samples was satisfactory.

4.5.3 Organic Constituent Analyses

All organic analyses of the samples from tank 241-T-111 were performed at PNNL. An EPA contract-laboratory-procedure-type organics-speciation analysis was performed on the core composites. No levels of organic compounds above the contract required quantitation limit were found in any of the samples, and they were not expected to contribute to the sample matrix. The organic analyses performed were volatile organic analyses, semi-volatile organic analyses, total organic halides, and extractable organic halides. Duplicates were performed for all of these analyses. Table 4-5 lists the analyses and procedure numbers.

At the 222-S Laboratory, the initial total organic carbon (TOC) assays were done using a furnace oxidation procedure of a water digested sample. At PNNL, the TOC content for the solids was determined using the hot persulfate method. That method dissolves a sample in a 90 °C+ sulfuric acid solution to liberate inorganic carbon (carbonate). $K_2S_2O_8$ is then added, and organic carbon is converted to CO_2 , which is measured coulometrically. As stated in the "Executive Summary," these methods did not provide satisfactory results for the tank 241-T-111 waste samples. Later, furnace oxidation tests done at PNNL gave results much higher than those from the 222-S Laboratory and more in line with the observed exothermic activity.

Table 4-4. Analytical Methods for Chemical and Radionuclide Analyses.

Analyte	Method	Procedure number
Hg	Cold vapor atomic absorption	LA-325-102
F ⁻ , Cl ⁻ , NO ₃ ⁻ , NO ₂ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	Ion chromatography	LA-533-105
CN ⁻	Distillation/spectrometric analysis	LA-695-101 LA-695-102
U	Laser fluorimetry	LA-925-106
Total Alpha Total Beta	Proportional counting	LA-508-101
²³⁸ Pu, ^{239/240} Pu, ²⁴¹ Am	Alpha spectrometry	LA-503-156
²³⁷ Np	Alpha proportional counting	LA-933-141
Total Cations	Inductively coupled plasma	LA-505-151
⁹⁰ Sr	Beta proportional counting	LA-220-101
⁹⁹ Tc ⁷⁹ Se ¹⁴ C ³ H	Liquid scintillation	LA-438-101 LA-365-132 LA-348-104 LA-218-114
¹²⁹ I ⁵⁹ Ni	Low energy gamma analysis	LA-378-104 PNL-ALO-464
⁶³ Ni	Liquid scintillation	PNL-ALO-474
¹⁵⁴ Eu, ¹⁵⁵ Eu, ²⁴¹ Am, ¹³⁷ Cs, ⁶⁰ Co	Gamma energy analysis	LA-548-121
NO ₂ ⁻	Spectrophotometry	LA-645-001
H ⁺	pH	LA-212-103
As Se	Graphite furnace atomic absorption	PNL-ALO-214 PNL-ALO-215
Pu Isotopic	Fusion mass spectrometry	PNL-ALO-423 PNL-MA-597
U Isotopic	Mass spectrometry uranium laser	PNL-MA-597 PNL-ALO-445
TOC	Total organic carbon	LA-344-105 PNL-ALO-380 PNL-ALO-381
CO ₃ /C	Total inorganic carbon	LA-622-102

Table 4-5. Analytical Methods For Organic Analytes.

Analysis	Method	Procedure Number
Volatile organic analysis	Gas chromatography/mass spectrometry	PNL-ALO-335
Semi-volatile organic analysis	Gas chromatography/mass spectrometry	PNL-ALO-345
Extractable organic halides	Microcoulometric titration	PNL-ALO-320,2
Total organic halides	Microcoulometric titration	PNL-ALO-321

4.5.4 Segment-Level Analyses

The objectives of segment-level analyses are to provide (1) information as a function of depth pertaining to the overall waste energetics (water content and chemical reactivity) and (2) the particle size distribution and other general rheological information. To accomplish these goals, the limited suite of analyses listed in Table 4-6 were performed on each homogenized segment. These analyses were conducted using the analytical procedures identified in Tables I5-1 and I5-2 of WHC-EP-0210, Rev. 3 (Hill et al. 1991). In addition, where appropriate, the information obtained from the segment-level homogenization tests will be used to enhance the interpretation of the data.

Table 4-6. Segment-Level Analysis.

Direct	Acid dissolution*
Thermogravimetric analysis differential scanning calorimetry Wt% H ₂ O particle size**	Inductively coupled plasma (metals) gamma energy analysis (¹³⁷ Cs) total alpha

*Acid dissolution assays were performed on the homogenization test segments.

**Particle size was done on non-homogenized segment material.

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5.0 ANALYTICAL RESULTS: TANK 241-T-111

5.1 CHEMICAL ANALYSES

5.1.1 Analytical Results: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Online inter-element corrections were performed for matrix interferences. The ICP has a built-in correction capability to adjust for moderate matrix interferences; however, there may be performance degradation on samples containing weight-percent quantities of iron, aluminum, or uranium. Corrections were made for moderate levels of aluminum, calcium, chromium, and magnesium in the samples. Corrections were made for high iron concentrations as well. Process or preparation blank values have not been subtracted from the results. In the water digestion and liquid grab sample assays, the single most prevalent element is sodium by at least an order of magnitude. Relative percent differences (RPD) for water digestion results were high for some analytes (i.e., above the 20 percent acceptance criteria), but there was no consistent trend observed between cores 31 and 33.

In the fusion assays, some elements can appear to be at high concentrations because of the large dilution factors required for fusion samples. These high dilution factors propagate errors. Those analytes actually may be present only in concentrations marginally above the detection limit. For several analytes, higher quantitation was found in the acid digestion results. For purposes of determining inventories and making comparisons, the highest reliable average analytical result will be used between acid and fusion preparations.

In reviewing the data, a subtle bias or gradient was observed between the results for cores 31 and 33, with core 31 having slightly higher values overall than core 33. Although not readily discernable among the first tier analytes (sodium, bismuth, iron, and phosphorus), the difference between cores 31 and 33 is more evident in the second tier analytes (aluminum, lead, and magnesium). The RPDs between the individual core composite samples and their replicates were small, suggesting that the gradient is real and not an analytical artifact, however, this observation could be the result of the compositing procedure. There were nine segments used in the core 33 composites, but only eight segments in the core 31 composites (segment 6 was absent in core 31). Furthermore, sample variability may contribute or be wholly responsible for the observed difference.

RPDs for most elements were within the 20-percent acceptance criteria for acid and fusion results, and generally were less than 10 percent for the major analytes. Potential sample contamination for boron and silicon exists because of the caustic nature of the samples and the glass vials used to store the samples in the laboratory; however, silicon routinely demonstrated a low bias. Calcium and magnesium for blank and spike recovery results may have been biased high by the powder used on the analysts' gloves when performing the assays. With the small sample sizes used in the assay, even trace amounts of powder have the potential to impact the analyses. Low spike recoveries were noted for several analytes for differing reasons. Silver recoveries are commonly low because of the precipitation of

silver chloride in the sample digestion. Poor spike recoveries of iron, magnesium, and calcium accompany high preparation blank results, but the overall correlation is poor. Spike failures frequently are noted for major elements when the spike concentration is insignificant compared to the analyte concentration in the waste matrix. Spike and standard results outside the acceptance criteria for these analytes do not necessarily invalidate the sample results for the ICP in general, or for those analytes in particular. Individual analyte failures need to be evaluated on a case by case basis. All of these behaviors could affect, and are considered in the interpretation of the results.

The detection limit for each analyte is provided for comparison with the results to aid in interpretation. All ICP analytes are reported in the data tables; however, those consistently contributing significant (i.e., generally greater than approximately 0.2 weight percent) amounts to the composition of the waste matrix generally are relevant to bulk characterization. The fusion/acid ratio, which can be compared in the table, for most analytes indicates near total dissolution for the acid digestion assay. Average values for the analytes are reported to three significant figures. The full range of ICP analytical results can be found in the full data packages (McKinney et al. 1993). All reported concentration values are based on grams of wet sample, unless otherwise specified. Table 5-1 provides ICP analyte concentration information on the core composites as a function of the sample preparation. Table 5-2 provides ICP analyte concentrations as a function of depth for core 33. Table 5-3 compares the water digestion core composite ICP values with the results from the grab sample.

Core 31

The most significant analytes measured by the water digestion of the core composite were sodium and phosphorous (probably as a soluble phosphate), and sulfur (probably as a soluble sulfate). Much smaller amounts of iron, chromium, and silicon also were measured. RPDs were elevated for these samples (between 10 and 20 percent), but were generally within the 20-percent acceptance criteria. For analytes with results outside the acceptance criteria, no clear trend between the two composites can be established. The water digestion result for core 31, composite 1 had several analytes with high RPDs, many of which are significant contributors to the waste: iron, lead, manganese, silver, bismuth, lanthanum, and strontium. Core 31, composite 2 had few analytes with results outside the acceptance criteria: barium, calcium, lead, and vanadium. All of the analytes noted are largely insoluble and that characteristic probably is contributing to the observed variability.

The results from the acid digestion preparation of the core composite samples had sodium, phosphorous, sulfur, calcium, chromium, iron, manganese, bismuth, and lanthanum as major analytes. RPDs are very good in general for most of the major analytes (generally between 5 and 10 percent), well within the 20 percent acceptance criteria. Analytes outside the acceptance criteria for core 31, composite 1 were antimony and boron (56 percent and 27 percent, respectively). However, neither of those analytes are substantial contributors to the waste matrix, and for analytes near the detection limit, reproducibility is not expected.

Table 5-1. ICP Cations. (4 pages)

Analyte	Acid-water digestion	Fusion digestion	Prep type	Core 31 comp. 1	Core 31 comp. 2	Core 33 comp. 1	Core 33 comp. 2
	Detection limit	Detection limit		Average concentration	Average concentration	Average concentration	Average concentration
	($\mu\text{g/g}$)	($\mu\text{g/g}$)		($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)
Al	2.4		Water	6.71	10.3	15.5	11.0
			Acid	584	705	472	405
		12.0	Fusion	644	693	484	459
Sb	17.7		Water	17.7	17.7	17.7	17.7
			Acid	30.4	36.5	35.9	22.6
		85.5	Fusion	88.6	88.3	109	88.4
As	3.0		Water	3.0	3.0	2.99	3.0
			Acid	3.15	2.92	3.45	3.06
	3.3		GFAA ¹	3.3	3.3	3.3	3.2
		15.0	Fusion	15.0	15.0	15.0	15.0
Ba	0.3		Water	0.305	0.416	0.547	0.516
			Acid	57.0	64.9	66.8	87.3
		1.5	Fusion	58.8	60.6	65.4	73.7
Be	0.1		Water	0.10	0.10	0.10	0.10
			Acid	0.105	0.097	0.117	0.104
		0.5	Fusion	0.501	0.499	0.499	0.499
Cd	0.4		Water	0.40	0.40	0.4	0.4
			Acid	7.22	7.86	4.4	3.72
		2.0	Fusion	8.25	10.7	6.42	7.17
Ca	4.4		Water	50.8	61.6	66.4	67.5
			Acid	2,200	2,480	1,490	1,350
		22.0	Fusion	2,760	2,660	2,220	2,050
Cr	0.9		Water	209	229	224	211
			Acid	1,860	1,840	2,060	2,140
		4.5	Fusion	1,890	1,700	1,790	1,820
Co	0.8		Water	0.8	0.825	0.821	0.825
			Acid	3.4	7.16	3.13	2.91
		4.0	Fusion	10.1	10.8	13.3	11.8
Cu	0.4		Water	0.4	0.4	0.4	0.4
			Acid	25.2	79.6	16.4	13.0
		2.0	Fusion	36.3	34.2	22.1	24.6

Table 5-1. ICP Cations. (4 pages)

Analyte	Acid-water digestion	Fusion digestion	Prep type	Core 31 comp. 1	Core 31 comp. 2	Core 33 comp. 1	Core 33 comp. 2
	Detection limit	Detection limit		Average concentration	Average concentration	Average concentration	Average concentration
	($\mu\text{g/g}$)	($\mu\text{g/g}$)		($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)
Fe	1.0		Water	79.6	140	132	159
			Acid	19,200	20,000	17,500	17,300
		5.0	Fusion	20,500	19,600	15,900	16,100
Pb	6.2		Water	7.05	7.93	6.24	6.19
			Acid	475	543	201	168
		31.0	Fusion	440	484	267	269
Mg	0.3		Water	2.94	3.95	3.84	3.83
			Acid	435	479	305	290
		1.5	Fusion	438	443	268	272
Mn	0.2		Water	14.7	25.1	25.4	33.8
			Acid	6,190	6,140	6,710	6,280
		1.0	Fusion	6,380	5,940	6,220	6,590
Ni	1.7		Water	1.7	1.7	1.7	1.7
			Acid	151	157	110	108
		8.5	Fusion	NR	NR	NR	NR
K	11.2		Water	734	783	712	648
			Acid	1,100	1,210	1,210	1,020
		56.0	Fusion	NR	NR	NR	NR
Se	7.6		Water	7.6	8.01	7.58	7.59
			Acid	7.98	7.4	10.3	7.79
		1.5	GFAA	1.5	1.5	1.5	1.5
		38.0	Fusion	38.0	37.9	38.0	38.0
Ag	0.5		Water	0.639	1.16	0.553	0.499
			Acid	203	227	44.3	30
		2.5	Fusion	214	221	39.5	37.1
Na	3.1		Water	34,000	35,000	30,800	32,000
			Acid	37,600	38,700	35,000	36,300
		15.5	Fusion	39,800	39,000	33,900	35,200
V	0.5		Water	0.5	0.707	0.5	0.8
			Acid	12.7	21.4	13.9	9.99
		2.5	Fusion	12.1	16.5	15.3	14.7

Table 5-1. ICP Cations. (4 pages)

Analyte	Acid-water digestion	Fusion digestion	Prep type	Core 31 comp. 1	Core 31 comp. 2	Core 33 comp. 1	Core 33 comp. 2
	Detection limit	Detection limit		Average concentration	Average concentration	Average concentration	Average concentration
	($\mu\text{g/g}$)	($\mu\text{g/g}$)		($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)
Zn	0.3	1.5	Water	0.3	0.3	0.3	0.3
			Acid	79.4	101	44.2	35
			Fusion	104	106	105	110
Bi	7.5	37.5	Water	115	191	231	270
			Acid	23,600	23,300	28,500	28,400
			Fusion	20,900	20,100	26,500	26,700
B	0.6	3.0	Water	3.31	3.19	5.54	4.25
			Acid	27.1	23.4	29.4	32.2
			Fusion	3.0	2.99	4.84	4.84
Ce	10.1	50.5	Water	10.1	10.1	10.1	10.1
			Acid	32.6	28.6	37.8	35.8
			Fusion	50.6	50.4	50.4	50.4
La	1.4	7.0	Water	6.02	8.52	13.8	15.8
			Acid	3,720	3,620	4,640	4,890
			Fusion	3,690	3,410	4,510	4,810
P	5.8	29	Water	5,760	5,960	5,300	5,700
			Acid	10,100	9,960	9,860	11,300
			Fusion	11,600	11,100	9,070	9,910
Si	1.3	6.5	Water	438	560	669	620
			Acid	482	471	528	394
			Fusion	5,960	5,840	5,460	5,410
Sr	0.3	1.5	Water	1.21	2.13	2.18	2.34
			Acid	282	280	305	334
			Fusion	303	280	291	317
S	2.7	13.5	Water	1,190	1,200	1,060	1,140
			Acid	1,230	1,260	1,140	1,220
			Fusion	1,350	1,310	1,080	1,160
Sn	1.6	8.0	Water	1.6	1.6	1.6	1.6
			Acid	4.21	2.44	1.81	1.61
			Fusion	8.01	7.98	7.99	7.99

Table 5-1. ICP Cations. (4 pages)

Analyte	Acid-water digestion	Fusion digestion	Prep type	Core 31 comp. 1	Core 31 comp. 2	Core 33 comp. 1	Core 33 comp. 2
	Detection limit	Detection limit		Average concentration	Average concentration	Average concentration	Average concentration
	($\mu\text{g/g}$)	($\mu\text{g/g}$)		($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)	($\mu\text{g/g}$)
Ti	0.4		Water	0.4	0.4	0.4	0.4
			Acid	29.4	33	8.9	6.46
		2.0	Fusion	72.9	72.4	22.3	24.1
Zr	NR		Water	0.8	0.799	0.798	0.798
			Acid	0.84	0.778	0.913	0.816
		NR	Fusion	4.00	3.99	4.00	4.00
Hg	0.125	NR	CVAA ²	1.59	1.83	1.20	1.08

NR = Not reported

¹GFAA: Graphite furnace atomic absorption²CVAA: Cold vapor atomic absorption.

Table 5-2. Tank 241-T-111 Core 33 ICP Selected Analyte Trending as a Function of Depth (Acid prep on segments).

Segment	Ca ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Na ($\mu\text{g/g}$)	Bi ($\mu\text{g/g}$)	La ($\mu\text{g/g}$)	P ($\mu\text{g/g}$)	Si ($\mu\text{g/g}$)	S ($\mu\text{g/g}$)
1	4,800	490	17,300	23,900	240	22,400	760	3	4,400	380	800
3	1,100	1,200	11,700	3,800	70	25,800	24,200	3,900	4,800	430	720
5	1,300	2,000	16,100	2,800	90	32,100	33,400	5,100	9,100	400	1,100
7	1,100	2,500	18,100	4,200	70	36,000	34,700	4,900	12,200	450	1,200
9	950	2,000	16,600	4,600	90	40,700	24,100	4,200	15,300	450	1,400

Table 5-3. Grab Sample/Water Digestion Data--ICP Average Values.

Analyte	Grab sample avg. concentration ($\mu\text{g/g}$ sample)	Core 31, comp. 1 ($\mu\text{g/g}$ sample)	Core 31, comp. 2 ($\mu\text{g/g}$ sample)	Core 33, comp. 1 ($\mu\text{g/g}$ sample)	Core 33, comp. 2 ($\mu\text{g/g}$ sample)
Ca	< DL	51	62	66	68
Cr	230	210	230	220	210
Fe	< DL	80	140	130	160
Ni	< DL	15	25	25	34
Na	24,800	34,000	35,000	30,800	32,000
Bi	< DL	120	190	230	270
La	< DL	6	9	14	16
P	3,200	5,800	6,000	5,300	5,700
Si	60	440	560	670	620
S	750	1,200	1,200	1,100	1,100

< DL = below detection limit.

This behavior is true in general for analytes with these characteristics. The silicon RPD is marginal at 19.26 percent, but acceptable. For core 31, composite 2, cobalt, copper, silicon, and tin were outside the acceptance criteria. Again, cobalt, copper, and tin were not significant contributors to the waste, and thus have little influence on the interpretation of the data. The only clear trend for this assay is for silicon. The variation observed for silicon was attributed to the solubility of the waste matrix (i.e., the waste is not completely solubilized by the acid), and therefore, the fusion results will be reviewed to quantitate silicon. Based on a ratio of the acid and water digestion results, most of the analytes are not water soluble, except as noted earlier, however, approximately 10 percent of the chromium is water soluble.

The results from the fusion preparation core composite had sodium, phosphorous, bismuth, manganese, lanthanum, silicon, iron, calcium, and chromium as major analytes. Nickel was detected in substantial quantities, but the results are considered unreliable because of sample contamination (the method uses a nickel crucible to perform the fusion), and nickel was not detected in significant quantity in the acid digestion assay. RPDs were quite low, generally less than eight percent for most analytes, demonstrating excellent agreement. The only analyte with an RPD outside the acceptance criteria for core 31, composite 1 was cadmium, which is not a large contributor to the waste and is near the detection limit. The only analytes with excessive RPDs for core 31, composite 2 were cadmium and nickel. Both of these analytes have problems associated with them that make these results suspect for this test method (proximity to the detection limit for cadmium and cross-contamination from the

crucible for nickel). Comparisons with the acid digestion results indicate that the samples were well dissolved by the acid preparation, but in some cases, and with silicon especially, the fusion dissolution was necessary to obtain reliable, quantitative results for the analyte.

Core 33

Sodium, phosphorus (probably as a soluble phosphate), and sulfur (probably as a soluble sulfate) were the most significant analytes measured by the water digestion of the core composite. Much smaller amounts of iron, chromium, and silicon were the other main analytes. RPDs were elevated for these samples (between 10 and 20 percent), but generally were within the 20 percent acceptance criteria. For analytes with results outside the acceptance criteria, no clear trend between the two composites or between cores can be established firmly, but there was some correspondence between the cores and their respective composites (i.e., there was some agreement between cores 31 and 33 composite 1, etc.), but the connection was quite tenuous. The water digestion result for core 33, composite 1 had several analytes with high RPDs, many of which are significant contributors to the waste. These analytes are aluminum, barium, iron, manganese, bismuth, and lanthanum. For core 33, composite 2, only calcium and vanadium were outside the acceptance criteria. The degree of variability observed for this particular sample preparation is not unexpected. Most of these analytes probably are in a form that is not readily water soluble and, depending on the sample matrix exposure to the solution media, substantial differences may be observed.

The results from the acid digestion preparation of the core composite samples are quite similar to core 31. They had sodium, phosphorous, sulfur, calcium, chromium, iron, manganese, bismuth, and lanthanum as major analytes, the RPDs decline significantly in comparison to the water digestion results, both in the number of analytes outside the acceptance criteria and the overall magnitude of the RPDs themselves. The RPDs are very good in general for most of the major analytes (between 5 percent and 10 percent), well within the 20 percent acceptance criteria. Analytes outside the acceptance criteria for core 33, composite 1 were antimony and selenium (88.5 percent and 33.0 percent, respectively). For core 33, composite 2, antimony and silicon were outside the acceptance criteria (31.2 percent and 48.7 percent, respectively). The results for antimony and selenium are not surprising. They are not far above their respective detection limits and neither is a substantial contributor to the waste matrix. The silicon RPD result is not unexpected, because the waste has solubility properties that make it resistant to acid digestion, making this assay marginal at best. Based on a ratio of the acid and water digestion results, most of the analytes are not water soluble, except as noted earlier; however, approximately 10 percent of the chromium is water soluble. In this case, for several analytes, some consistency is seen between composite replicates and cores. As noted earlier, core 33 sample results are, in several cases, about 25 percent or more lower than core 31. Significant changes in analyte concentration were observed in the ICP acid digestion results as a function of depth for core 33. The results are shown in Table 5-2. The changes observed for some analytes are notable, ranging from factors of 3 and 4 for calcium, chromium, and phosphorous to orders of magnitude for manganese, bismuth, and lanthanum. These swings in concentration suggest the waste is heterogenous on a tank-wide scale and that the waste in the tank is layered.

Properties and major analytes for the fusion digestion results are similar to core 31, however the differences observed between the analytical results of cores 31 and 33 become much less consistent with this group of assay results. RPDs were generally low, less than 12 percent, with most analyte results substantially less than that. Antimony, calcium, and boron had RPDs outside the acceptance criteria for core 33, composite 1. In core 33, composite 2, cobalt and nickel, which are not large contributors to the waste, had RPDs outside the acceptance level and antimony, boron, and cobalt are near their respective detection limits. Several of these analytes have problems associated with them that make these results suspect for this test method. However, the variation seen for calcium is not expected and there is no reason for its behavior. In this case, no consistency was observed between composites or cores, except for nickel in cores 31 and 33, composite 2, and the nickel results for this test method are suspect.

5.1.2 Analytical Results--Anion Assays

Core 31 Ion Chromatography Results:

Major anions detected are NO_3^- and PO_4^{3-} , with smaller, but still substantial amounts of F^- and SO_4^{2-} . Nitrite and chloride are minor contributors to the waste. Indeed, the IC results for nitrite are considered an estimated result; however, the magnitude and range of concentration is confirmed by a spectrophotometric analysis. All RPDs for quantitated results are well within the 20 percent acceptance criteria, and generally are less than 10 percent. Comparisons of phosphorous and sulfur water-digestion ICP results with ion-chromatography results for PO_4^{3-} and SO_4^{2-} give good agreement (RPDs are less than 10 percent) and show that phosphorous is about 48 to 56 percent soluble (as phosphate) and sulfur is about 90 to 100 percent soluble (as sulfate). Table 5-4 illustrates the comparison between the water digestion ICP and IC results, and the relationship to the total amount of phosphorous and sulfur in the matrix. Table 5-5 presents the summary results for the IC analytes and other anions.

Core 33 Ion Chromatography Results:

Major analytes were the same as those found in core 31. RPDs for the minor analytes, F^- , Cl^- , and NO_2^- , were much higher in composite 1 than in composite 2, or in either of core 31's composites, exceeding 15 percent, but within the 20 percent acceptance criteria. Core 33, composite 2 had superior RPDs, all were less than 8 percent. Comparison of the phosphorous and sulfur water-digestion ICP results with IC for PO_4^{3-} and SO_4^{2-} gives good agreement, however, phosphorous shows a higher, but still acceptable variability, with RPDs of 13 to 17 percent, than sulfur as SO_4^{2-} , with RPDs of -1.4 to -3.3. Phosphorous is approximately 50 percent soluble as phosphate, whereas sulfur as sulfate is almost entirely soluble. Table 5-4 illustrates the comparison between the water digestion ICP and IC results, and the relationship to the total amount of phosphorous and sulfur in the bulk tank matrix. Note the ICP results are converted to phosphate and sulfate for comparison.

Table 5-4. Comparison of Ion Chromatography and Water Digestion ICP Results for Selected Analytes.

Sample ID	PO ₄ ³⁻ Concentration (μg/g)		PO ₄ ³⁻ RPD	SO ₄ ²⁻ Concentration (μg/g)		SO ₄ ²⁻ RPD	PO ₄ ³⁻ Solubility*		SO ₄ ²⁻ Solubility*	
	(IC)	(ICP.w)		(IC)	(ICP.w)		(IC)	(ICP.w)	(IC)	(ICP.w)
Core 31-C1	16,200	17,300	6.7	3,690	3,570	-3.3	50.8	54.2	100.4	97.1
Core 31-C2	17,400	17,900	2.8	3,740	3,600	-3.7	54.5	56.1	101.8	97.9
Core 33-C1	13,600	15,900	16.9	3,290	3,420	-3.3	42.6	49.8	89.5	93.1
Core 33-C2	15,100	17,100	13.2	3,470	3,660	-1.4	47.3	53.6	94.4	99.6

*Solubility is a ratio of the IC/ICP.w result to 31,900 μg/g PO₄³⁻ and 3,675 μg/g SO₄²⁻, the tank average of the converted fusion results.

ICP.w = Notation for ICP water digestion result.

Table 5-5. Anion Results--Composite Data (water leach).

Analyte	Detection limit (μg/g)	Core 31 (μg/g)		Core 33 (μg/g)		Grab sample (μg/g)
		Composite 1	Composite 2	Composite 1	Composite 2	Average
NO ₃ ⁻	100	44,300	43,800	36,900	40,100	30,300
PO ₄ ³⁻	100	16,200	17,400	13,600	15,100	8,400
SO ₄ ²⁻	100	3,690	3,740	3,290	3,470	2,900
Cl ⁻	10	470	497	401	432	490
F ⁻	10	3,090	3,130	1,370	1,630	2,100
NO ₂ ⁻	50	952	525	878	817	1,320 (IC)
TOC*	500	3,490	3,990	2,000	3,000	420
TIC*	500	650	824	823	950	670
Free OH ⁻	NM	NM	NM	NM	NM	3,000
pH*	NA	10.18	9.93	10.05	9.77	11.65
NH ₃ /NH ₄ ⁺	4,500	< DL	< DL	< DL	< DL	400

Table 5-5. Anion Results--Composite Data (water leach).

Analyte	Detection limit ($\mu\text{g/g}$)	Core 31 ($\mu\text{g/g}$)		Core 33 ($\mu\text{g/g}$)		Grab sample ($\mu\text{g/g}$)
		Composite 1	Composite 2	Composite 1	Composite 2	Average
Direct Cyanide ¹	5	< DL	< DL	< DL	< DL	< DL

NM = No measurement

NA = Not applicable

< DL = Below detection limit

Note: All IC results are obtained from a water leach preparation and are reported on a wet basis.

¹Direct Cyanide, $\text{NH}_3/\text{NH}_4^+$, pH, TOC, and total inorganic carbon (TIC) are not IC analyses, but are grouped with the anions for convenience. NO_2^- results reported are from spectrophotometric methods. At the 222-S Laboratory, TOC and TIC assays were done on water digested samples. When 325 performed segment level assays for these analytes, they did them on direct solid samples.

Core 31 and 33 Additional Anion Results:

- Nitrite, as determined from spectrophotometry, has good agreement between composites and acceptable RPDs. Concentrations between cores are observed to agree well also.
- The pH of the solids is measured using a water dilution of a solids aliquot. The pH of the mixture is measured and reported. The results for tank 241-T-111 waste from this method are consistent, ranging from 9.8 to 10.5, but are of limited utility because the sample preparation and assays only marginally represent the conditions in the tank. The pH as determined from a grab sample taken in 1994 (Simpson 1994, Appendix C) is between 11.5 and 11.8, and is considered more reliable and more representative of the waste tank conditions.
- Ammonia/ammonium results for the solids were all below the detection limit for the method. This is not unexpected. Over time, ammonia probably was slowly released to the vapor space and removed by passive ventilation. A small amount of this analyte remains in the liquids, but the liquid is being removed.
- TOC results indicate a substantial difference between cores 31 and 33 (core 31's TOC concentration is 33 percent higher than core 33's), but results for the individual core composites are very consistent. Core 31 composite 1 and composite 2 RPDs are negligible. Core 33, composite 1 and composite 2 RPDs are low, well within the acceptance criteria, but noticeable.

-
- TIC results were a factor of three to four times lower than the TOC results and were near the detection limit. Therefore, they are not considered wholly reliable, however the results did provide acceptable reproducibility. TOC results are also considered questionable, especially when contrasted with the calorimetry results from segment-level data from both cores (segments 1-3 particularly), and a furnace oxidation value of 4.1 weight percent (dry), for core 33, segment 2 (Baldwin 1994).

The gradient observed in the ICP results remains noticeable for the anions, especially for TOC and F⁻, but the overall effect is much less pronounced. This effect is expected and ascribed to the nature of the assay (i.e., water digestion assay results for soluble analytes in a mostly water matrix are expected to be reasonably homogeneous). TOC and F⁻ probably are present in insoluble forms, and thus are not as amenable to detection and are more likely to exhibit variations in concentration.

5.2 ANALYTICAL RESULTS--RADIOCHEMISTRY

5.2.1 Radiochemistry Assays--General Comments

Analyses appear to be consistent. Total beta measurements calculated using ⁶⁰Co detector efficiencies are largely in agreement with the sum of the major beta emitters, ⁹⁰SrY and ¹³⁷Cs [i.e., beta emission values must be adjusted by 1.42 and 1.51, respectively, the ratio of ⁹⁰SrY and ¹³⁷Cs to ⁶⁰Co detector efficiencies (Winters 1991)]. However, the total alpha values show only marginal agreement with the sum of the neptunium, plutonium, and americium/curium values. This behavior was attributed to the low activity of the samples and a recently discovered equipment problem. Technicians at the 222-S Laboratory identified an electronic problem with their alpha detection system involving the degree of discrimination between beta and alpha emissions. These two conditions are thought to contribute to the observed high bias of the total alpha measurements. Detection and quantitation of ¹³⁷Cs and most other radionuclides was based on the presumed ability of the fusion sample preparation to completely dissolve the waste. Water preparation samples were done on selected analytes as directed in the test plan. GEA measurements show good agreement with alpha energy analysis for ²⁴¹Am. GEA analytical values are not corrected to account for decay, however most of the radionuclides present are long-lived enough and low enough in concentration so that any correction at this point would be modest.

5.2.2 Gamma Energy Analysis Results

The GEA data from the replicate samples of the core composites for cores 31 and 33 prepared by caustic fusion agree reasonably well with each other (RPDs generally were within 10 percent). However, there is a discernable gradient between cores 31 and 33 for ¹³⁷Cs. This follows the general pattern observed for several other analytes, but in this case ²⁴¹Am does not appear to be affected. Review of the segment-level homogenization data for core 33 indicates that in general, the ¹³⁷Cs content is lowest in the bottom segments and

highest in the upper segments, increasing in concentration from bottom to top. This behavior indicates that the ^{137}Cs is concentrated in the upper portion of the tank. However, the overall radionuclide content of tank 241-T-111 is extremely low. The ^{154}Eu and ^{155}Eu content is above the detection limits only in segments 1 and 3, suggesting that these isotopes are in the upper portions of cores 31 and 33. However because of the limited segment level data, too many conclusions should not be drawn from these observations. Grab sample results for ^{137}Cs is more than a factor of four lower than those obtained from fusion assays, indicating that the radionuclides, ^{137}Cs in particular, are very insoluble. Agreement between the same top and bottom aliquots in the homogenization check samples prepared by acid digestion were very good for analytes above the detection limit, with RPDs generally less than 10 percent and usually much less than that, indicating sample homogeneity and/or relatively complete dissolution.

5.2.3 Total Alpha Analysis and Uranium Assay

Total alpha, plutonium, ^{237}Np , ^{241}Am , and ^{244}Cm analyses were performed on the fusion prepared samples of the core composites and selected assays were done on the liquid grab sample. Total alpha measurements were also performed on the homogenization check samples from segments 1, 3, 5, 7, and 9 from core 33. The total alpha activity was determined by drying a small aliquot of prepared sample on a counting plate and assayed with an alpha proportional counter. The plutonium and americium fractions were separated by solvent extraction or ion exchange and similarly counted.

The plutonium analyses are reported as total alpha $^{239/240}\text{Pu}$. The process blank was two to three orders of magnitude lower than the samples, indicating little contamination occurred during sample preparation. The total alpha concentration frequently tends to be somewhat lower than the sum of the individual alpha emitters. The difference is probably caused by absorption by the salt residue on the counting mounts. However, in this case, substantial differences are observed between the total alpha measurements and the sum of the individual alpha emitters. The total alpha emissions are believed to be lower than the measurement indicates because of a bias caused by beta emissions confounding the detector. The activity of the samples is so low that the offset used to discriminate between alpha and beta plateaus was not sufficient to provide accurate readings. Furthermore, analyses from PNNL indicate a potential low bias for plutonium in the samples. The degree of discrepancy ranges from over a factor of two to nearly a factor of five. This degree of disagreement warrants further attention. Isotope content was determined by thermal-ionization mass spectroscopy. Little variation in the plutonium isotopic composition was observed between cores. Total alpha measurements vary widely as a function of depth, but exhibit a general decreasing trend the deeper the samples are in the waste. Segment 5 was an exception to this trend. The anomalous total alpha reading in segment 5 may be indicative of a process upset or change in waste management operations, such as the 5-6 waste that Anderson (1990) notes was co-mingled with the 2C waste in 1952.

Uranium measurements were obtained from laser fluorimetry of the fusion-prepared sample from the two core composites and their replicates. The assays show good agreement between duplicates for each individual core composite, but there is not good agreement between the

core 31 and 33 replicates. Additionally, the gradient observed in the other assays is not evident here. Furthermore, analyses from PNNL indicate a potential low bias for uranium in the samples. The degree of discrepancy is nearly a factor of two for corresponding samples, and thus warrants further study. Differences in concentration as a function of the water content of the samples is not deemed to be an issue because the additional characterization work done in resolving the energetics question indicates that little or no water is lost while the samples are stored. Time lag is also not considered relevant, since the difference in time between the two assays was small in comparison to the half-lives involved. No general trend of the uranium concentration as a function of depth can be established because there is no segment-level data for this analyte.

5.2.4 Total Beta

Total beta, ^{90}Sr , and ^{99}Tc analyses were performed on the liquid grab sample and fusion prepared samples of the core composites. The total beta activity was determined by drying a small aliquot of prepared sample on a planchet and assaying it with a beta proportional counter. The ^{90}Sr fraction was separated by solvent extraction or ion exchange and counted. The ^{99}Tc fraction was separated similarly, but assayed using liquid scintillation. There generally is good agreement (RPDs were less than 10 percent) between duplicates, and preparation blank beta activities are orders of magnitude lower than the levels found in the samples, again indicating little contamination from preparation in the hot cell. Most of the beta activity in the tank samples is from ^{90}Sr and ^{137}Cs . There is also a trace of ^{99}Tc . The ^{90}Sr , ^{99}Tc , and ^{137}Cs data are consistent between the fusion core composites and their replicates, but in this case the gradient between cores 31 and 33 is observed for ^{90}Sr and ^{137}Cs . There is no data to determine if ^{90}Sr content varies as a function of depth.

Tables 5-6, 5-7, 5-8, and 5-9 show the average radionuclide concentrations found in the core composite samples. Table 5-10 shows average fission product concentration and total alpha concentrations as a function of depth.

Table 5-6. Consolidated Radionuclide Concentration Results for 241-T-111.

Analyte method	Detection limit	Core 31, composite 1	Core 31, composite 2	Core 33, composite 1	Core 33, composite 2
GEA analytes	($\mu\text{Ci/g}$)	($\mu\text{Ci/g}$)	($\mu\text{Ci/g}$)	($\mu\text{Ci/g}$)	($\mu\text{Ci/g}$)
$^{60}\text{Co.f}$	(DL = 4.07E-04)	< DL	< DL	< DL	< DL
$^{137}\text{Cs.f}$	(DL = 3.70E-04)	0.211	0.237	0.114	0.103
$^{154}\text{Eu.f}$	(DL = 1.20E-03)	0.00108	0.00324	< DL	< DL
$^{155}\text{Eu.f}$	(DL = 5.95E-04)	< DL	< DL	0.00307	< DL
$^{241}\text{Am.f}$	(DL = 1.14E-04)	0.0459	0.0409	0.0387	0.0443

Table 5-6. Consolidated Radionuclide Concentration Results for 241-T-111.

Analyte method	Detection limit	Core 31, composite 1	Core 31, composite 2	Core 33, composite 1	Core 33, composite 2
Beta emitters					
Total beta.f	(DL = 9.35E-02)	20.6	21.5	9.59	8.83
Total beta	Calculated	20.7	21.5	10.5	9.9
³ H.w	(DL = 3.15E-04)	< DL	< DL	< DL	< DL
¹⁴ C.w	(DL = 2.25E-04)	< DL	< DL	< DL	< DL
⁵⁹ Ni.a	(DL = 4.00E-06)	8.3E-05	3.33E-05	4.44E-05	4.07E-05
⁶³ Ni.a	(DL = 4.00E-06)	0.0093	0.00358	0.00545	0.00459
⁷⁹ Se.f	(DL = 1.40E-04)	< DL	< DL	< DL	< DL
⁹⁰ Sr.f	(DL = 2.15E-03)	7.16	7.43	3.65	3.43
⁹⁹ Tc.f	(DL = 4.60E-03)	0.00514	0.00473	0.0114	0.0104
¹²⁹ I.f	(DL = 6.40E-03)	< DL	< DL	< DL	< DL
Uranium and transuranics					
Total U.f (μg/g) (325)	(DL = 3.40E-02)	2,180 4,000	3,880 5,200	3,180 4,500	1,950 3,500
Total alpha.f	(DL = 7.01E-03)	0.358	0.359	0.377	0.379
Total alpha	Calculated (Range)	0.179-0.669	0.179-0.608	0.172-0.357	0.195-0.416
²³⁷ Np.f	(DL = 3.40E-02)	< DL	< DL	< DL	< DL
²³⁸ Pu.f	(DL = 1.00E-02)	< DL	< DL	< DL	< DL
^{239/240} Pu.f (325)	(DL = 3.50E-03)	0.138 0.628	0.136 0.565	0.134 0.319	0.147 0.368
²⁴¹ Am.f	(DL = 3.00E-03)	0.0414	0.0431	0.0382	0.0478
²⁴⁴ Cm.f	(DL = NR)	< DL	< DL	< DL	< DL

< DL = below detection limit

Analyte.f = fusion digestion

Analyte.a = acid digestion

Analyte.w = water digestion

NR = Not reported

Total beta calculated determined by: 1.42 (2)(⁹⁰Sr) + 1.51 (¹³⁷Cs)Total alpha calculated determined by: ^{239/240}Pu + ²⁴¹Am

Table 5-7. Core Composite Uranium.

Core number	U _{FL} (222-S) (μg/g)	U _{FL} (325) (μg/g)	²³⁸ U mass percent	²³⁵ U mass percent
Core 31, composite 1	2,180	4,000	99.3074	0.6755
Core 31, composite 2	3,880	5,200	99.3098	0.6761
Core 33, composite 1	3,180	4,500	99.3125	0.6761
Core 33, composite 2	1,950	3,500	99.3161	0.6717

FL = Uranium measurement by laser fluorimetry.

222-S Assay date: 4/92

325 Assay date: 9/92

Table 5-8. Plutonium Concentration and Isotopic Distribution.

Core number	Total Pu α (222-S) (μCi/g)	Total Pu α (325) (μCi/g)	²³⁸ Pu mass percent	²³⁹ Pu mass percent	²⁴⁰ Pu mass percent	²⁴¹ Pu mass percent	²⁴² Pu mass percent
Core 31, C1	0.138	0.628	0.005	96.7199	3.2109	0.0352	0.0151
Core 31, C2	0.136	0.565	0.0105	96.6351	3.2834	0.0496	0.0215
Core 33, C1	0.134	0.319	0.004	96.7540	3.1046	0.1071	0.0683
Core 33, C2	0.147	0.368	0.0105	96.5499	3.3436	0.0621	0.0337

222-S Assay date: 4/92

325 Assay date: 9/92

C1 = Composite 1

C2 = Composite 2.

Table 5-9. Radiochemical Analyses of Grab Sample.

Analyte	Average concentration (μCi/mL)	Average concentration (μCi/g) ¹
⁹⁰ Sr	0.001	0.001
¹³⁷ Cs	0.090	0.087
^{239/240} Pu	6.83E-05	6.58E-05
Total Alpha	0.0024	0.0023
Total Beta	0.233	0.224

¹Density of 1.036 g/mL used for conversion.

Table 5-10. Tank 241-T-111 Core 33 Radionuclide Analyte Trending as a Function of Depth (Acid prep on segments).

Segment	¹³⁷ Cs (μCi/g)	¹⁵⁴ Eu (μCi/g)	¹⁵⁵ Eu (μCi/g)	²⁴¹ Am (μCi/g)	⁶⁰ Co (μCi/g)	Total alpha (μCi/g)
1	0.403	0.021	0.027	0.138	0.006	0.649
3	0.140	9.05E-04	0.002	0.014	0.0005	0.166
5	0.088	< DL	< DL	0.020	< DL	0.527
7	0.023	< DL	< DL	0.014	0.0005	0.350
9	0.013	< DL	< DL	0.050	< DL	0.262

5.3 TANK 241-T-111 CORE SAMPLE RHEOLOGICAL/ PHYSICAL MEASUREMENTS

Physical and rheological assays consume substantial quantities of material. Tables 5-11 and 5-12 provide a breakdown of the total amount of sample available at the outset of the analytical effort. Figure 5-1 shows the location where the core samples were taken and the waste depth. Measurements of physical characteristics such as shear strength, viscosity, particle size, and settling properties were taken. These measurements are necessary for the design and fabrication of retrieval, pretreatment, and final waste disposal systems.

Rheological assays were performed on samples from core 31, segments 2, 4, and 8. Particle size measurements were done on each segment of core 31. The data from segment 4 is not considered valid for these assays because it had dried before the measurements were taken. The drying process irreversibly changed the physical properties of the sample under investigation, and thus the sample is not considered representative. Therefore, the results from most of these assays will not be presented. However, in some cases it is useful to compare and contrast the results from the "representative" samples with the samples that dried.

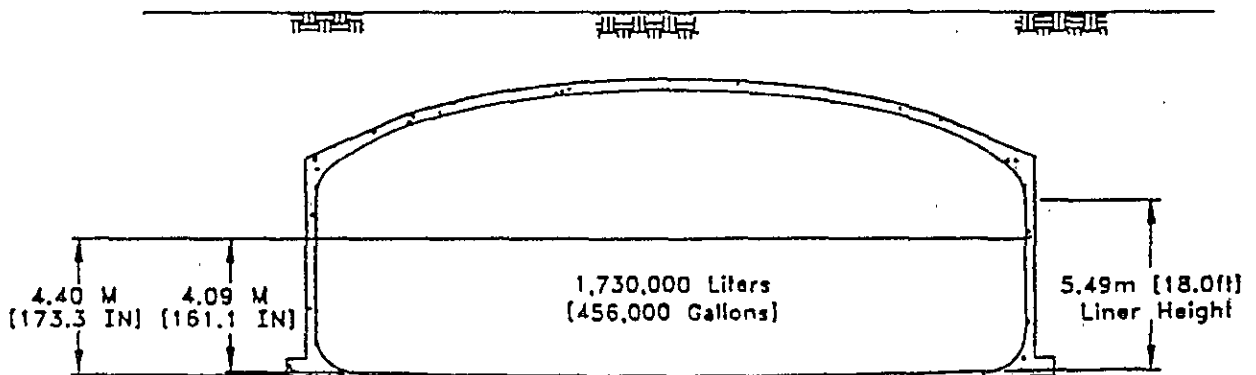
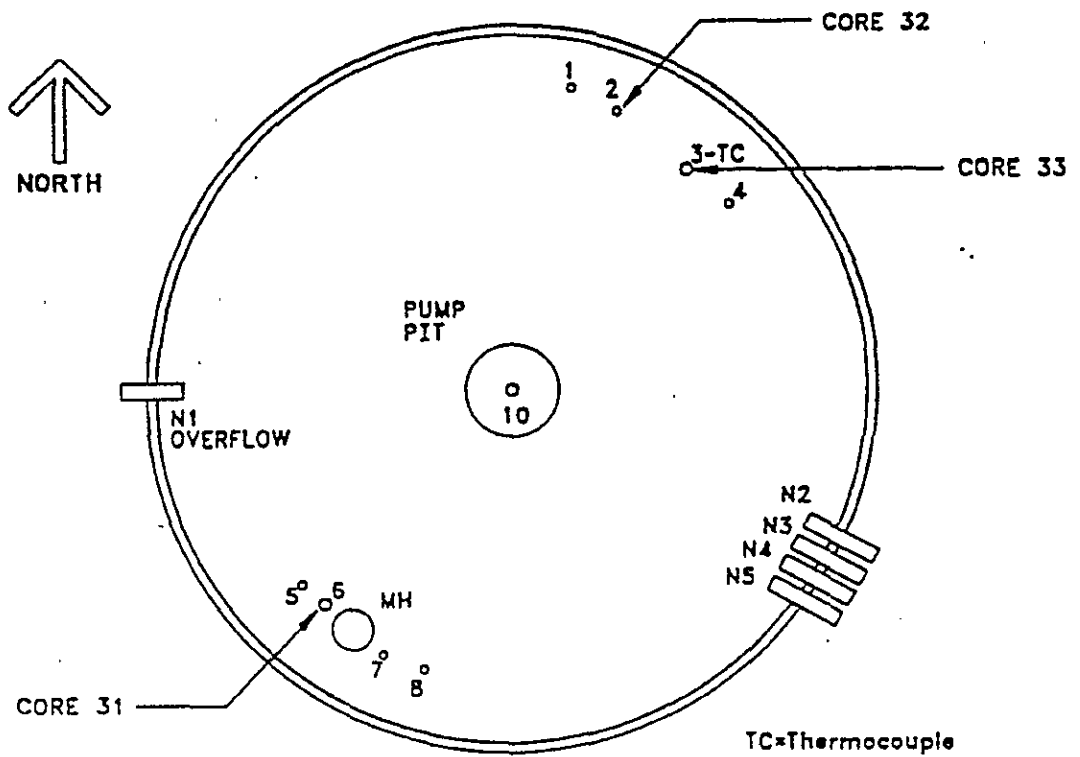
Table 5-11. Tank 241-T-111 Core Sample Description Summary.

Core number	Segment number	Solid sample mass (g)	Liquid sample mass (g)	Approximate solid sample volume (mL)	Liquid sample volume (mL)	Approximate solid sample length
31	1	18.74	45.26	Not Recorded	~ 50	Not Resolved
31	2	178.68	4.12	150	NA	15 in. (38 cm)
31	3	162.2	NA	177	NA	18 in. (46 cm)
31	4	153.47	NA	148	NA	15 in. (38 cm)
31	5	190.94	NA	187	NA	19 in. (48 cm)
31	6	0	NA	0	NA	No Sample
31	7	186.44	NA	177	NA	18 in. (46 cm)
31	8	186.44	NA	187	NA	19 in. (48 cm)
31	9	203.08	NA	187	NA	19 in. (48 cm)

Table 5-12. Tank 241-T-111 Core Sample Description Summary.

Core number	Segment number	Solid sample mass (g)	Liquid sample mass (g)	Approximate solid sample volume (mL)	Liquid sample volume (mL)	Approximate solid sample length
33	1	159.16	0	137	NA	14 in. (36 cm)
33	2	209.59	0	187	NA	19 in. (48 cm)
33	3	167.9	0	163	NA	16 in. (41 cm)
33	4	182.05	0	167	NA	16 in. (41 cm)
33	5	174.3	0	167	NA	17 in. (43 cm)
33	6	217.37	0	187	NA	19 in. (48 cm)
33	7	196.91	0	187	NA	19 in. (48 cm)
33	8	199.8	0	187	NA	19 in. (48 cm)
33	9	191.01	0	187	NA	19 in. (48 cm)

Figure 5-1. Current Condition of Tank 241-T-111.



5.3.1 Shear Strength

The shear strength of the waste from tank 241-T-111 was measured on the unhomogenized segment samples from core 31 (segments 2, 4, and 8). The shear strength measurements were made at ambient temperatures using a shear vane connected to a viscometer and rotated at 0.3 rpm. Shear strength (τ_s) is a semiquantitative measurement of the force required to move the sample. Because shear strength is dependent on sample handling, the measurement was taken without any sample homogenization. Small aliquots from the segments 2, 4, and 8 from core 31 were taken and assayed. The aliquots were transferred to a sample jar and allowed to settle for several weeks so that they could recover from the disturbance of sampling and extrusion. The extended delay between sample and analysis was permitted because it is believed that the longer the sample sits undisturbed, the closer it will resemble its original condition; therefore, the shear measurement is likely to be more representative. The shear stress (S_r) of the sample was recorded as a function of time and the shear strength was calculated using Equation 1.

$$\tau_s = \frac{[\% \tau / 100] * S_r * 4.9E+05}{\frac{\pi * H_v * D_v^2}{2} + \frac{\pi * D_v^3}{6}} \quad (1)$$

where

- $\% \tau / 100$ = The ratio of the total torque to the maximum torque of the viscometer head, measured as a percentage of the full scale on the plot of the shear stress versus time diagram (dimensionless)
- S_r = Instrument reading proportional to the torque (dimensionless)
- $4.9E+05$ = Maximum torque of the viscometer head (dyne•cm)
- H_v = Shear vane height (0.635 cm)
- D_v = Shear vane diameter (0.635 cm)

The shear strength for segments 2 and 8 were found to range $5,000 \pm 2,300$ dynes/cm². Segment 4 is not reported because of sample drying. Although relatively low, the shear stress of the material exceeded the baseline value for the measurement system (200 dynes/cm²). Therefore, the values are considered to be valid and representative. Some additional drying of the sample may have occurred during the settling time, causing the shear stress to be higher than expected.

5.3.2 Shear Stress and Viscosity as Functions of Shear Rate

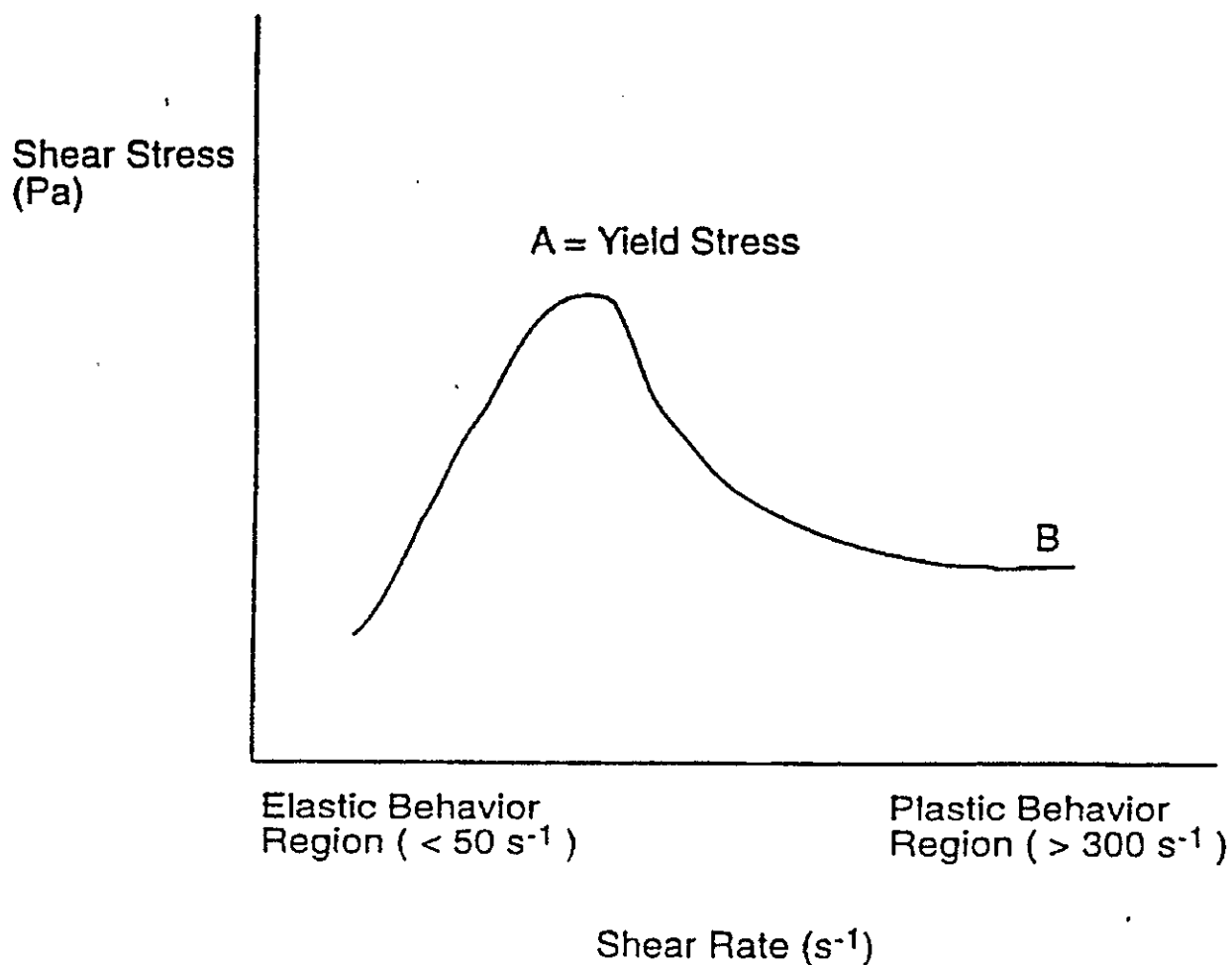
Shear stress measurements, as functions of shear rate, were performed on the as-received, 1 to 1 and 3 to 1 water to sample dilution of the sample at ambient hot-cell temperatures [ranging from 27 to 34 °C (81 to 93 °F)] and at 95 °C (203 °F). Drying the as-received sample at 95 °C posed difficulties in measurement; therefore no results of the rheograms for the samples run under those conditions are presented. In addition, the results from segment 4 are not presented because the drying that occurred compromised the sample properties, as discussed previously.

A rheogram for a material with a yield stress has two sections. The first section is a straight line beginning at the origin and climbing up the ordinate. This portion of the rheogram records the material as it acts like a solid or gel. When sufficient force is applied to the material to make it yield, the rheogram breaks sharply to the right; recording the material's behavior as a fluid. The point on the rheogram at which the sample's behavior transfers from a solid or gel to a fluid is the yield point or yield stress. This minimum shear stress must be exceeded to initiate fluid behavior. The tank wastes demonstrate both elastic and plastic behavior, depending on the amount of shear acting on them. The samples are elastic under low shear conditions (less than 50 s⁻¹), and plastic under high shear conditions (greater than 300 s⁻¹).

Viscosity measurements as a function of shear rate for the 1 to 1 diluted samples had viscosities near the limits of detection of the system (2 cP) for over the broad range of shear rates; however, some qualitative and quantitative information was obtained from the measurement trials. Even though the measurements were at the limits of detection, the qualitative and quantitative behavior was consistent and reproducible. Viscosity was observed to increase slightly, then decrease with increasing shear rates. The 1 to 1 dilution of the segment 2 and segment 8 samples exhibited tendencies toward yield-pseudoplastic behavior. In fact, the general behavior exhibited by the wastes is best described by a yield-pseudoplastic model, however the system was not modeled and empirical model parameters were not determined because the system was at the detection limits. No other measurements of the viscosity as a function of shear rate were made on the 1 to 1 dilution samples at 95 °C (203 °F) or the 3 to 1 dilution samples.

Figures 5-2 to 5-6 are general illustrations of the rheograms. They are not to scale and do not fully capture all of the nuances and detail that is contained in each measurement trial. However, when coupled with the description underneath each diagram, much insight can be obtained about the flow properties of the waste. If more detailed rheological information is required, the data package should be consulted. Note that in the figures, Point A is where the sample begins to register movement. Point B represents the behavior of the sample at the maximum shear rate of the viscometer.

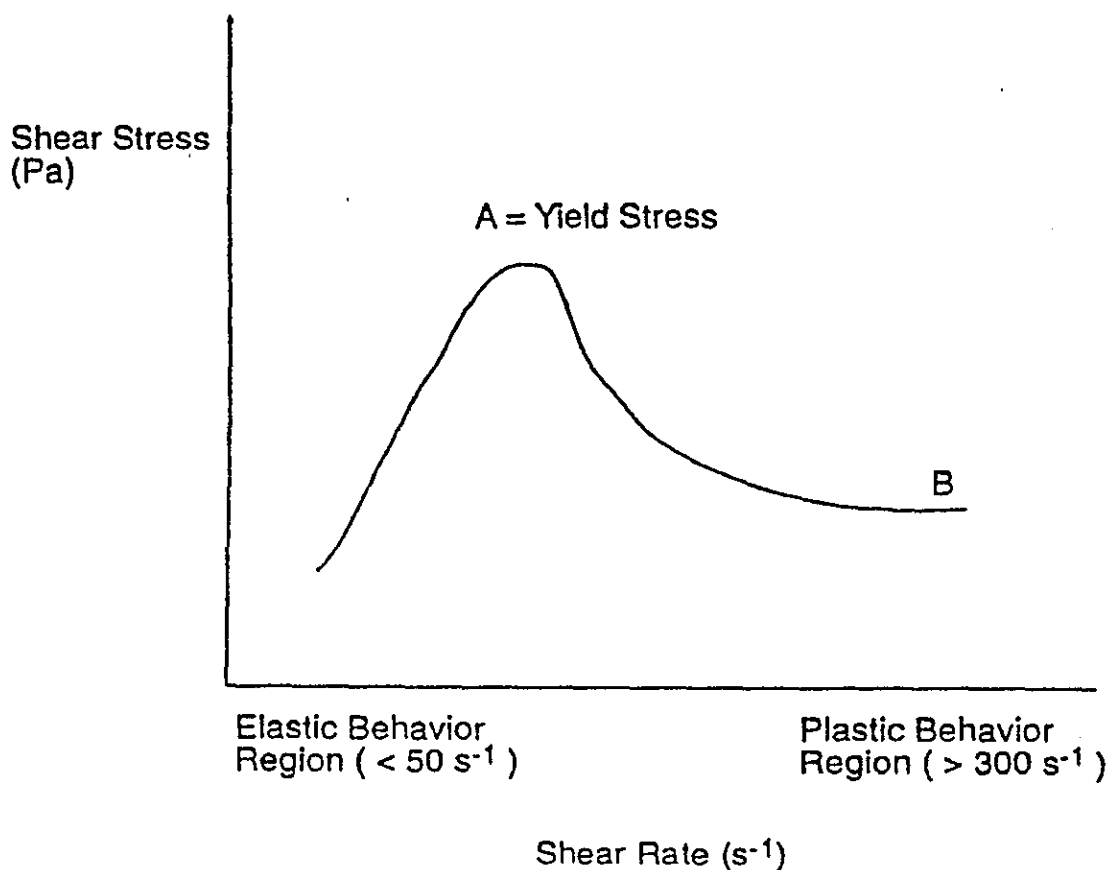
Figure 5-2. Shear Stress as a Function of Shear Rate: Direct Sample.



Shear Stress as a Function of Shear Rate: Direct Sample.

Sample: core 31	Sample number	Temperature (°C)	Point A shear stress range (Pa)	Qualitative behavior of rheogram	Point B shear stress (Pa)
Segment 2	80701	34	88 - 220	Wide variation at low shear, converging to a single value at high shear.	165
Segment 2	80703	33	200 - 680	Same	70
Segment 8	123201	33	36 - 108	Same	77
Segment 8	123202	33	0 - 108	Same	50

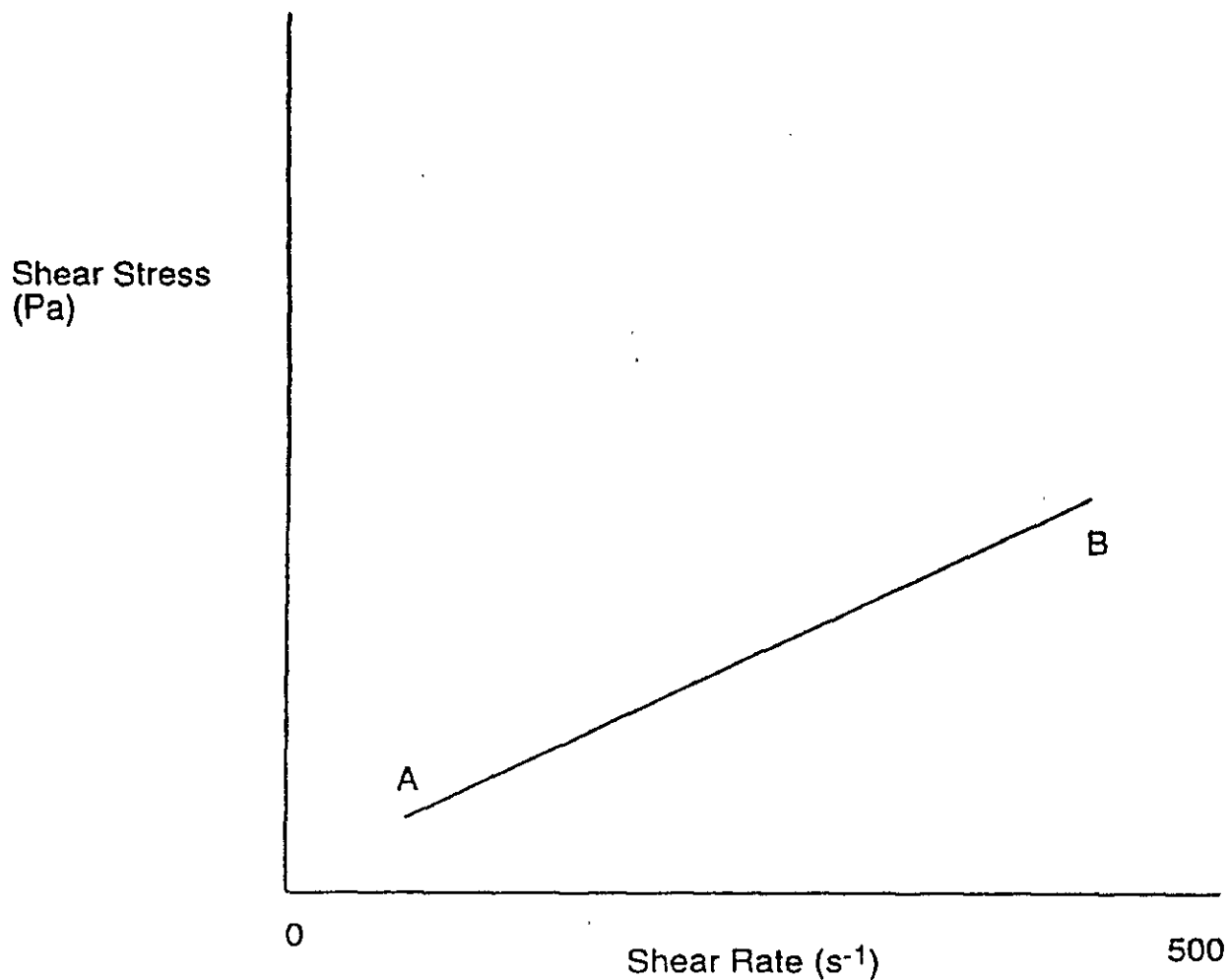
Figure 5-3. Shear Stress as a Function of Shear Rate: 1 to 1 Dilution, Water to Sample.



Shear Stress as a Function of Shear Rate: 1 to 1 Dilution, Water to Sample.

Sample: core 31	Sample number	Temperature (°C)	Point A shear stress range (Pa)	Qualitative behavior of rheogram	Point B shear stress (Pa)
Segment 2	1	27	0.6 - 4.2	Wide variation at low shear, converging to a single value at high shear.	2.4
Segment 2	2	27	1.2	Linear	2.8
Segment 2	3	95	1.0 - 7.0	Wide variation at low shear, converging to a single value at high shear.	2.0
Segment 2	4	95	0.7 - 1.1	Linear	1.2 - 1.4
Segment 2	5	95	1.0 - 2.4	Linear	2.2

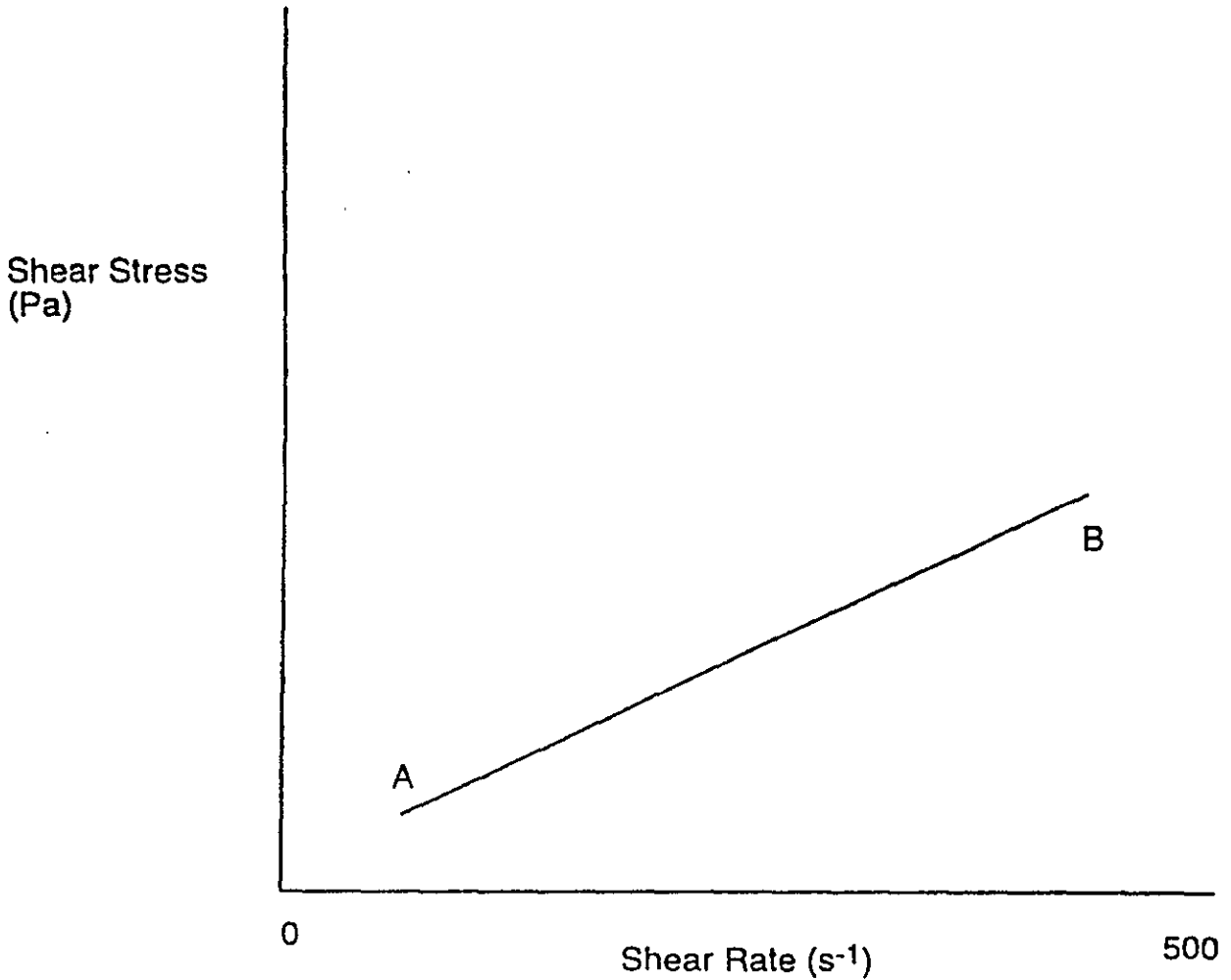
Figure 5-4. Shear Stress as a Function of Shear Rate: 1 to 1 Dilution, Water to Sample.



Shear Stress as a Function of Shear Rate: 1 to 1 Dilution, Water to Sample

Sample: core 31	Sample number	Temperature (°C)	Point A shear stress range (Pa)	Qualitative behavior of rheogram	Point B shear stress (Pa)
Segment 8	1	27	0.4 - 0.6	Linear	2.8
Segment 8	2	27	0.6	Linear	2.8
Segment 8	3	95	0.6	Linear	2.0
Segment 8	4	95	2.0 - 5.0	Erratic, non-linear	2.0
Segment 8	5	95	0.2	Linear	0.7 - 0.9

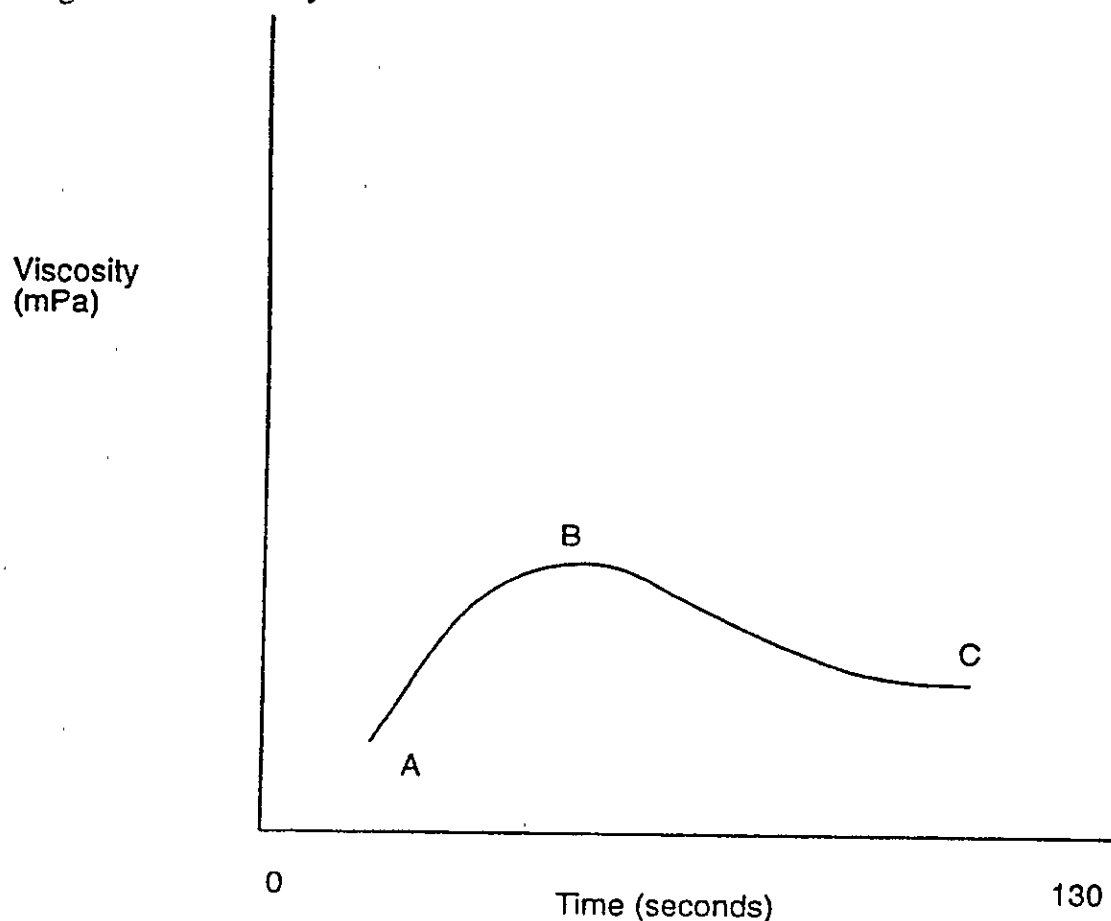
Figure 5-5. Shear Stress as a Function of Shear Rate: 3 to 1 Dilution, Water to Sample.



Shear Stress as a Function of Shear Rate: 3 to 1 Dilution, Water to Sample.

Sample: core 31	Sample number	Temperature (°C)	Point A shear stress range (Pa)	Qualitative behavior of rheogram	Point B shear stress (Pa)
Segment 2	1	27	0.05 - 0.25	Linear	0.75 - 1.1
Segment 2	2	27	0.2 - 0.35	Linear	1.2
Segment 2	3	95	0.2	Linear	0.8
Segment 2	4	95	0.3	Linear	1.0
Segment 8	3	95	Not defined	Erratic, non-linear	0.4
Segment 8	4	95	0.3	Linear	1.0

Figure 5-6. Viscosity as a Function of Time: 1 to 1 Dilution, Water to Sample.



Viscosity as a Function of Shear Rate: 1 to 1 Dilution, Water to Sample

Sample: core 31	Sample number	Temperature (°C)	Point A viscosity (mPa)	Qualitative description of rheogram	Point B viscosity (mPa)	Point C viscosity (mPa)
Segment 2	1	30	0.65	Rises, levels off, then gradually declines	1.8 - 2.0	1.5 - 1.7
Segment 2	2	30	0.56	Slightly sinusoidal	0.6	0.6
Segment 2	3	30	0.80	Rises, levels off, then gradually declines	1.0	0.9
Segment 8	3	30	0.75	Flattened exponential growth and decay curve	1.0	0.75
Segment 8	4	30	0.85	Flattened exponential growth and decay curve	0.95	0.9

5.3.3 Particle Size Measurement

Particle size is analyzed by placing a small amount of sample in a dispersant, which is the liquid used to disperse and suspend the particles from the solid sample. Samples from each segment of core 31 were prepared and assayed. The prepared sample was placed in a particle size analyzer. The apparatus measures particle size by passing a thin beam of laser light through the dispersant. The diameter of a particle in the dispersant can be determined by the amount of light that it blocks as it passes through the beam. The dimension measured by this method is the value across the short diameter of the particle. This means that if a particle is oblong, the machine estimates the shortest length across the particle. The term "diameter" throughout this text will be used to describe any linear profile of any shape.

An important consideration involving the analysis of particle size is the dispersant used. The primary concern involved with the dispersant is that it may dissolve the particle. Any particles existing in the tank that are soluble in the dispersant will dissolve or decrease in size during the analysis. Depending on the dispersant, the particle size analysis may not represent the true particle size distribution in the tank. In the case of tank 241-T-111, water was used as the dispersing medium. If a true particle size distribution is required, the mother liquor, or drainable liquid of the tank should be used if possible because the tank particulates are already in equilibrium with the tank's mother liquor. The insolubility of the waste matrix suggests that the particle size data acquired should be acceptable.

The mean particle size in the number distribution runs in a narrow range from 0.93 to 1.23 microns in diameter for tank 241-T-111 waste samples. Table 5-13 presents the summary results of the measurements.

Table 5-13. Core 31 Particle Size Distribution by Number.

Segment	Mean (μm)	Standard deviation	Median (μm)
1	1.23	0.89	0.94
2	1.13	0.80	0.88
3	1.17	1.00	0.91
4	0.93	0.60	0.80
5	0.95	0.63	0.81
6	-	-	-
7	0.97	0.60	0.83
8	1.02	0.85	0.82
9	1.02	0.83	0.83

Table 5-14 presents the summary results of the volume distribution measurements. Assuming that the density of the solid material within the tank is constant, the volume distribution is also the best estimation of the mass particle size distribution of the tank.

Table 5-14. Core 31 Particle Size Distribution by Volume.

Segment	Mean (μm)	Standard deviation	Median (μm)
1	28.56	35.92	5.81
2	14.91	20.76	4.79
3	64.99	46.19	58.69
4	24.87	34.15	5.63
5	37.87	47.91	12.31
6	-	-	-
7	7.95	11.88	4.02
8	24.72	28.18	10.02
9	59.69	49.04	58.97

The number density graph is plotted over the acquisition range of the device (from 0.5 to 150 microns). The numbers of particles in each size range, shown as a percentage of the whole, are graphed against their respective size ranges to form a distribution curve. The figures show that the modes for particle size range between the origin and 2.0 microns. In fact, over 80 percent of the measured particles fit within this narrow band. As with the number distribution, the volume distribution is represented by a probability volume density graph. The average particle size in the volume distribution is considerably larger than in the number distribution. The particle size in the volume distribution ranges over the full scale of the device, 0.0 microns to 150 microns in diameter, between the 8 segments (core 31 segment 6 was empty, but the nomenclature for the other samples held). The analyzer calculates particle volume as the cube of the diameter.

In core 31, approximately 70 percent of particle measurements for segments 1, 2, 4, 5, 7, and 8 fall into the range between 0.0 and 24.0 microns, and tend to be dispersed towards the smaller particle sizes. Segments 3 and 9 were exceptions to this rule. They had a distribution over the broad spectrum of particle sizes, with the particles generally much larger and more widely scattered over the 0.0 to 150.0 micron range and a slight tendency towards the smaller end of the scale. In segment 3, 23 percent of the particles were less than 24 microns. In segment 9, 40 percent of the particles were less than 24 microns.

The disparity between the segment measurements possibly indicates a difference in waste type, or perhaps a transitional layer between two waste types that individually are physically similar, but when commingled, may precipitate larger particulate materials. In segments 1, 2, 4, 5, 7, and 8, over 60 percent of the particles in the sample have a diameter of less than

24.0 microns. In segments 3 and 9, over 50 percent of the particles have a diameter of greater than 24.0 microns. In the retrieval and subsequent treatment of the tank wastes, it may be desirable to design pumping or filtration systems for the tank particulate. Therefore, the volume distribution of the particles should not be neglected (i.e., particles with diameters of over 20 microns should be considered in these designs). In addition, variation in particle size distribution is believed to have an impact on analytical precision, especially with small sample sizes, and thus, should be considered when evaluating analytical results. Plots of the probability number and volume density for each core are presented as Figures 5-7a to 5-14b.

5.3.4 Settling Behavior of As-Received and Diluted Samples

This section analyzes the settling behavior and physical properties of the grab samples and the as-received 1 to 1 and 3 to 1 water to sample dilutions. The physical properties reported here include settling rates and volume percent for settled solids and weight percent and volume percent for centrifuged solids. The experimental procedures used to take these measurements were reported previously (McKinney et. al 1993). The physical properties of the grab samples are reported in Table 5-15. The properties for core 31 samples are summarized in Table 5-16.

No settling was observed in the as-received segment samples over a period of three days, and there was no standing liquid obtained from the samples. Two dilutions of 1 to 1 and 3 to 1 water to sample ratios, respectively were prepared, and the volume-percent settled solids for each of the dilutions are plotted as a function of settling time.

The 1 to 1 dilution for segment 2 reaches a final volume percent settled solids of 85 to 87 percent. Settling is observed throughout the three-day period, but the majority of the settling is observed in the first 10 hours. The 3 to 1 dilution reaches a final volume-percent settled solids of approximately 52 percent. Again, settling is observed over three days, and the first 10 hours is when the majority of the solids settle. Qualitatively, the settling behavior for both sample dilutions is a steep, nearly linear relationship between the initial fluidization of the material and the first 10 hours of settling. After that, the final 10 percent of the suspended solids take up almost the rest of the time settling in a long, gradual decline, before coming to equilibrium.

The 1 to 1 and 3 to 1 dilutions for segment 4 were compromised by drying the sample before its assay. However, some observations and contrasts with the other samples are appropriate. Settling is mostly completed after 3 to 4 hours, and is complete after 10 hours. This is in sharp contrast to the other samples for which there is a long, asymptotic-like settling behavior observed for a substantial portion of the suspended solids (10 to 15 percent), after the initial settling phase. This behavior is suggestive of a colloid or gel for segments 2 and 8. In contrast, segment 4 appears to be a collection of discrete particles with no interaction between them.

Figure 5-7a. Core 31, Segment 1, Particle Size: Number Density.

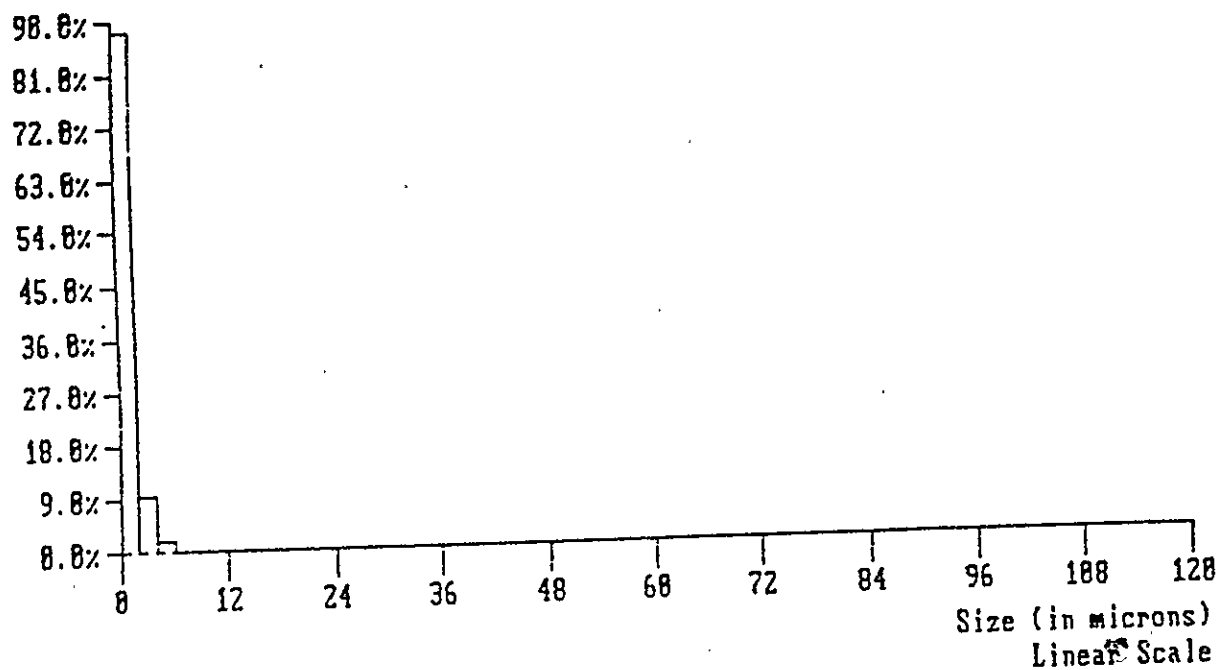


Figure 5-7b. Core 31, Segment 1, Particle Size: Volume Density.

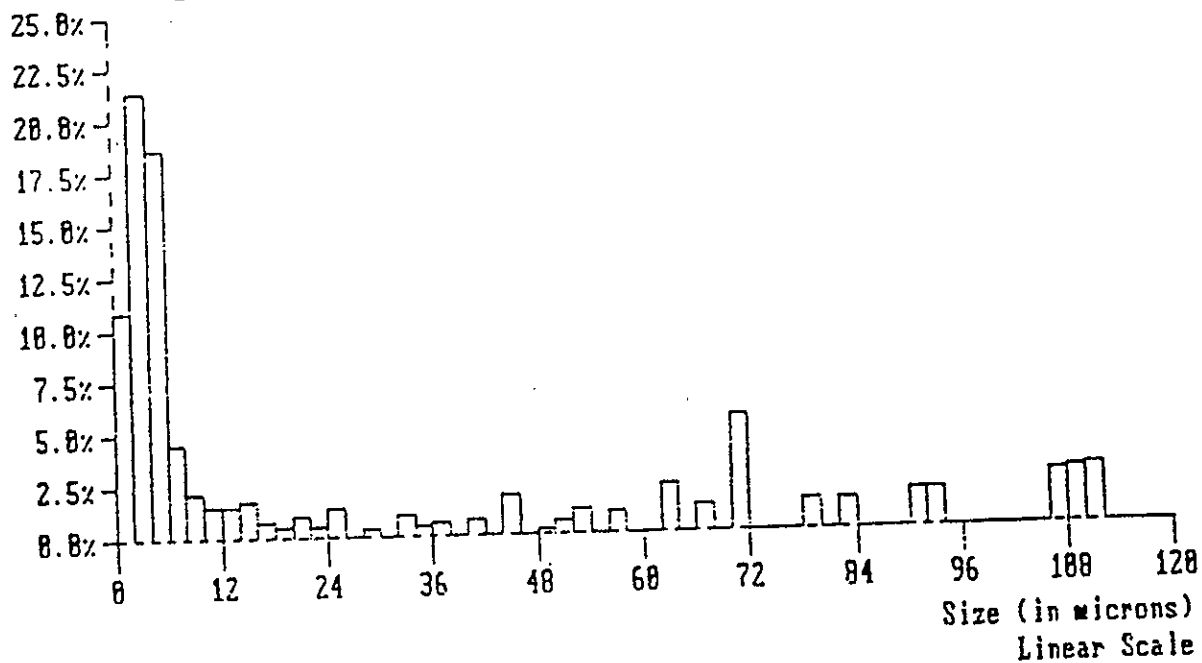


Figure 5-8a. Core 31; Segment 2, Particle Size: Number Density.

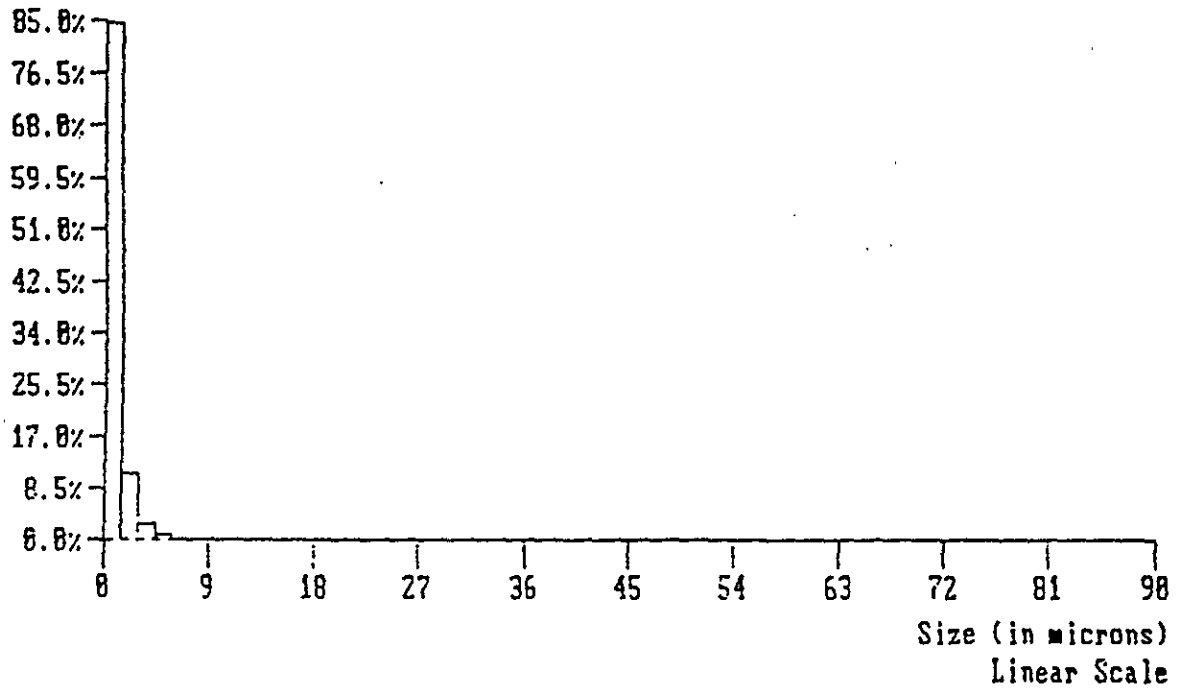


Figure 5-8b. Core 31, Segment 2, Particle Size: Volume Density.

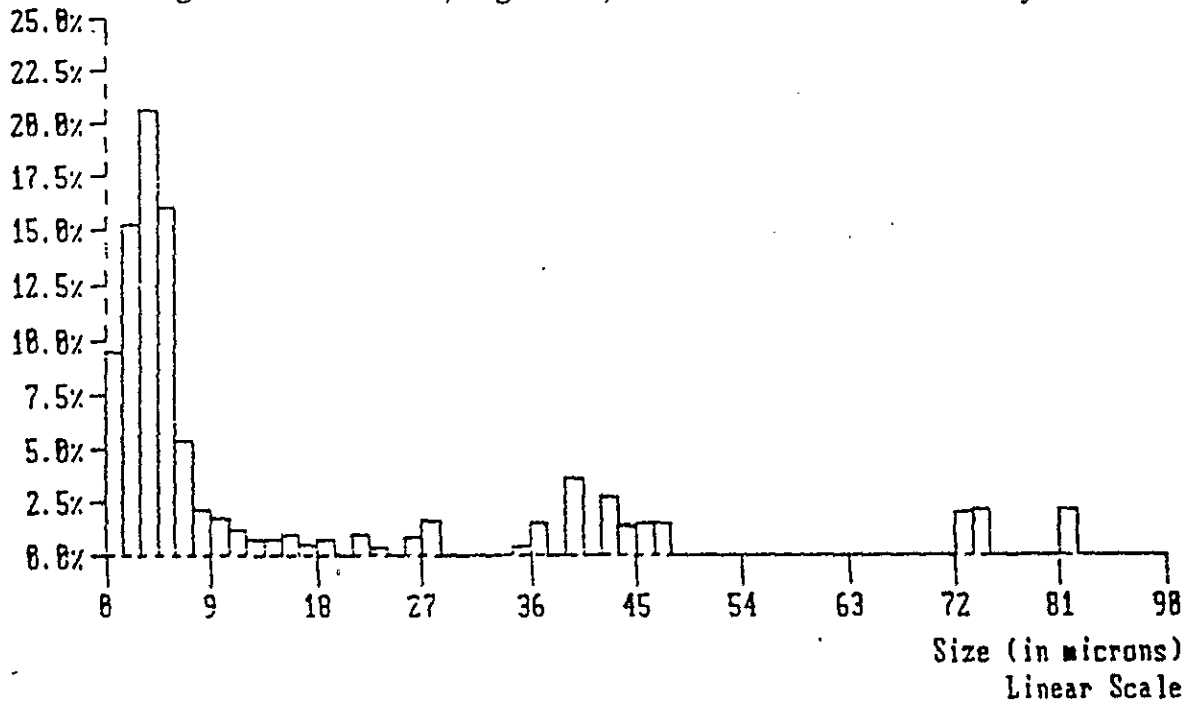


Figure 5-9a. Core 31, Segment 3, Particle Size: Number Density.

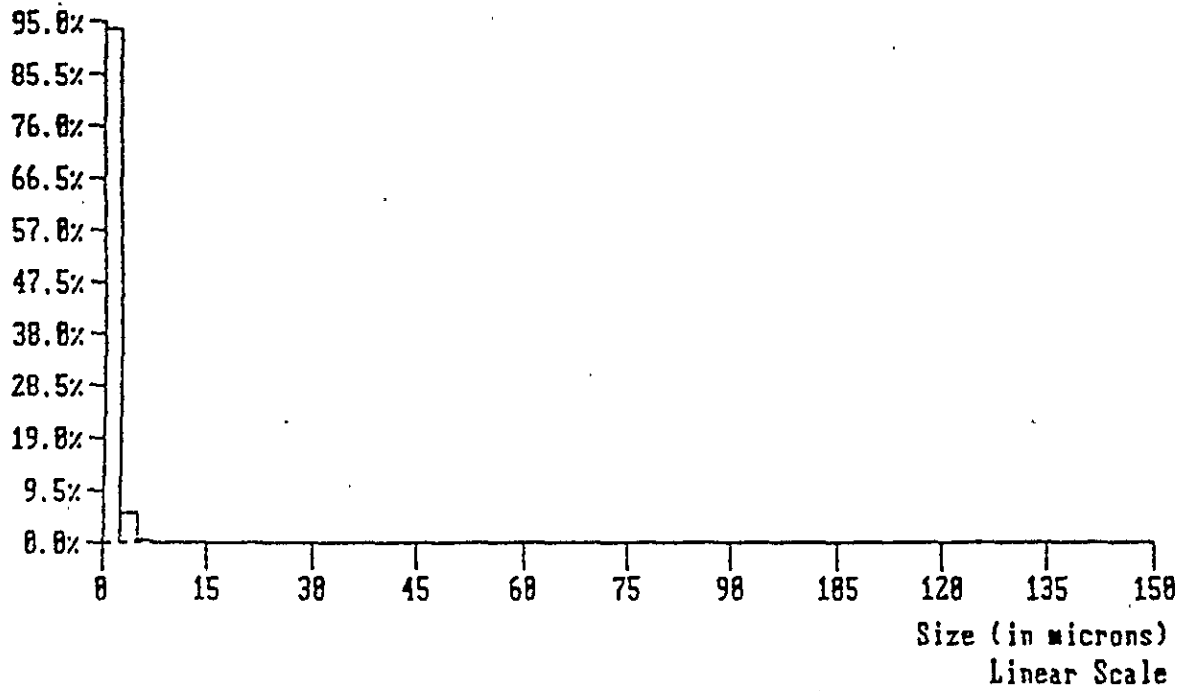


Figure 5-9b. Core 31, Segment 3, Particle Size: Volume Density.

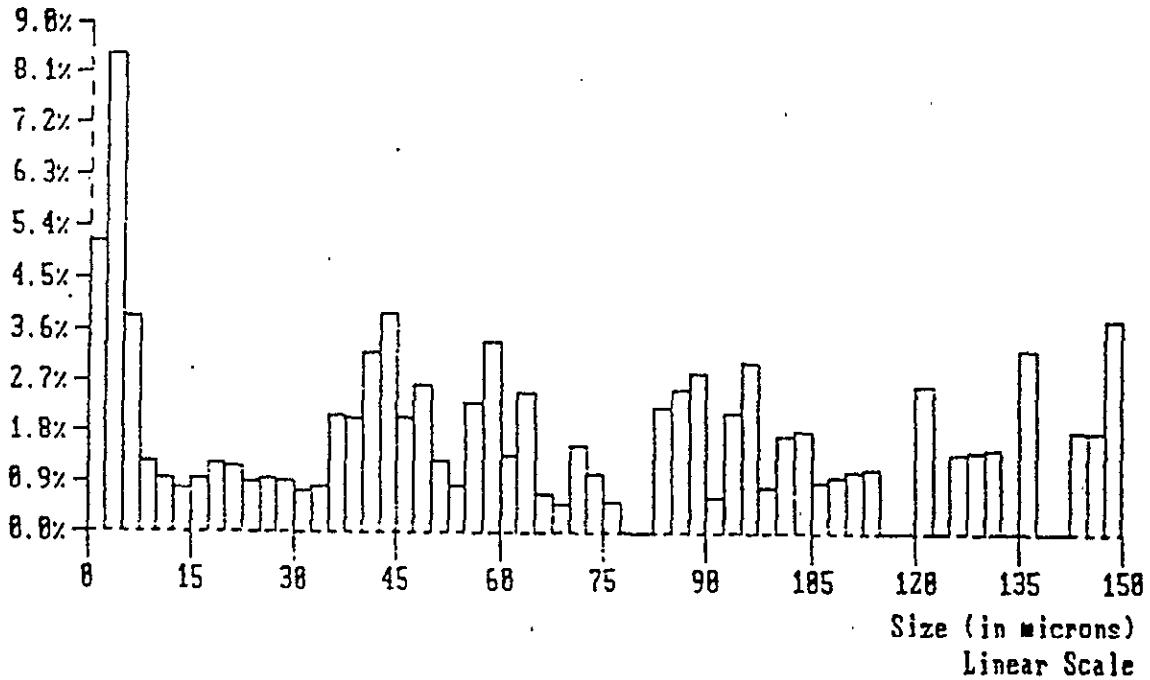


Figure 5-10a. Core 31, Segment 4, Particle Size: Number Density.

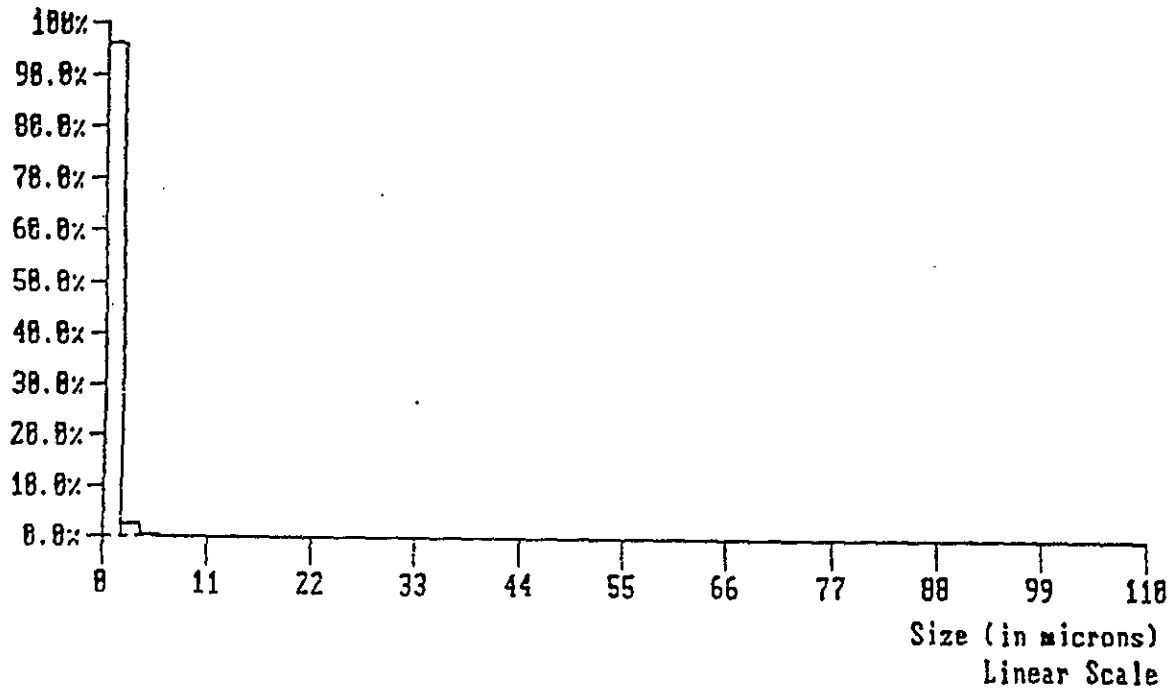


Figure 5-10b. Core 31, Segment 4, Particle Size: Volume Density.

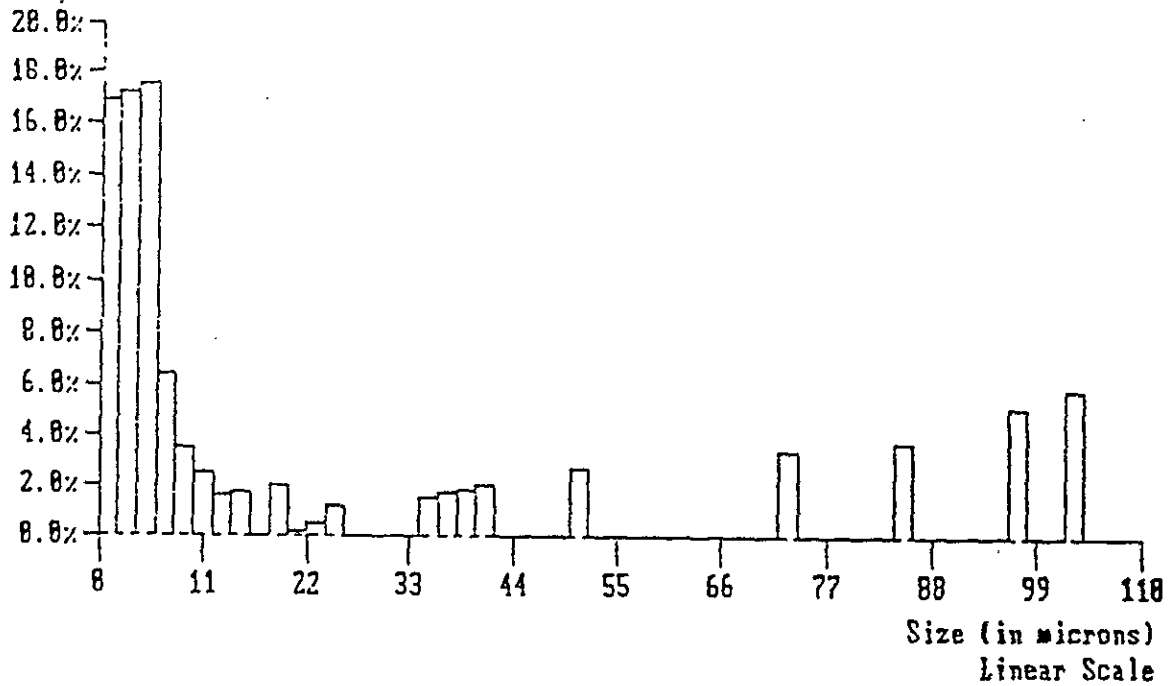


Figure 5-11a. Core 31, Segment 5, Particle Size: Number Density.

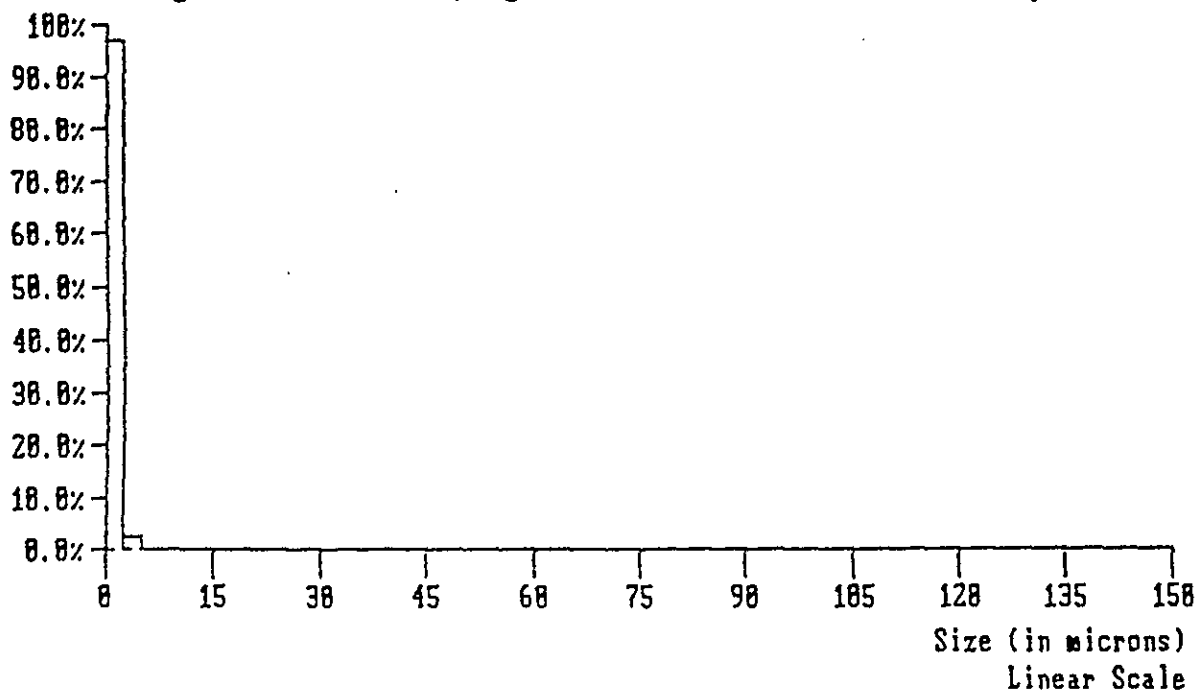


Figure 5-11b. Core 31, Segment 5, Particle Size: Volume Density.

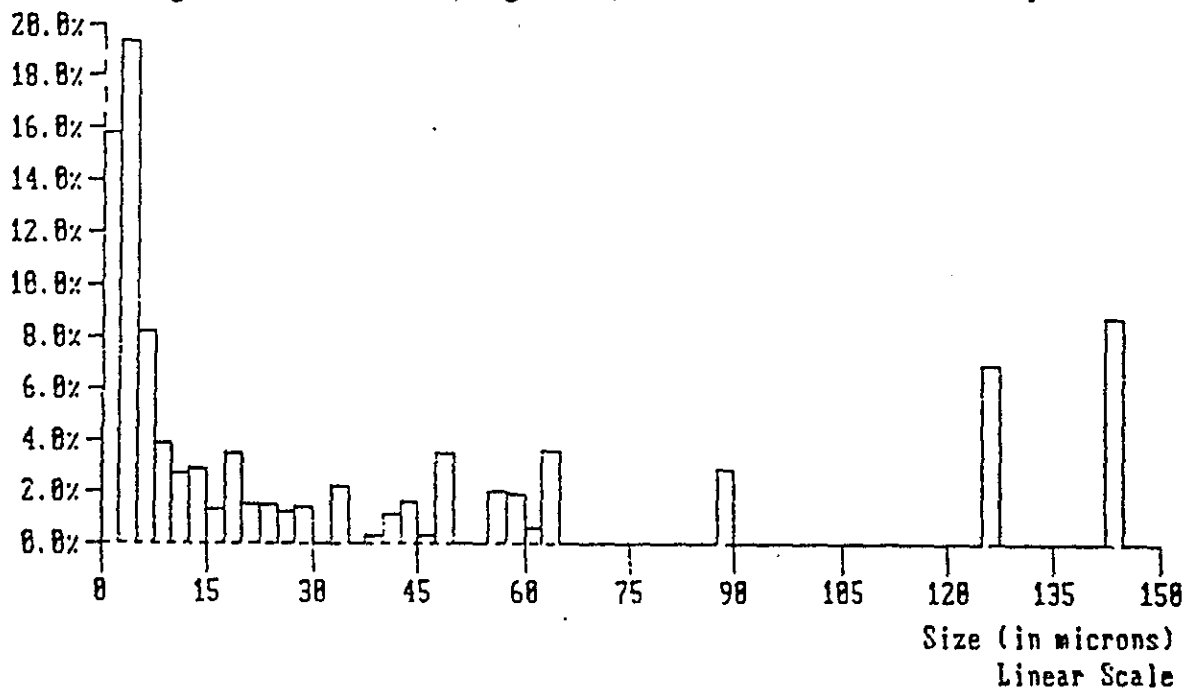


Figure 5-12a. Core 31, Segment 7, Particle Size: Number Density.

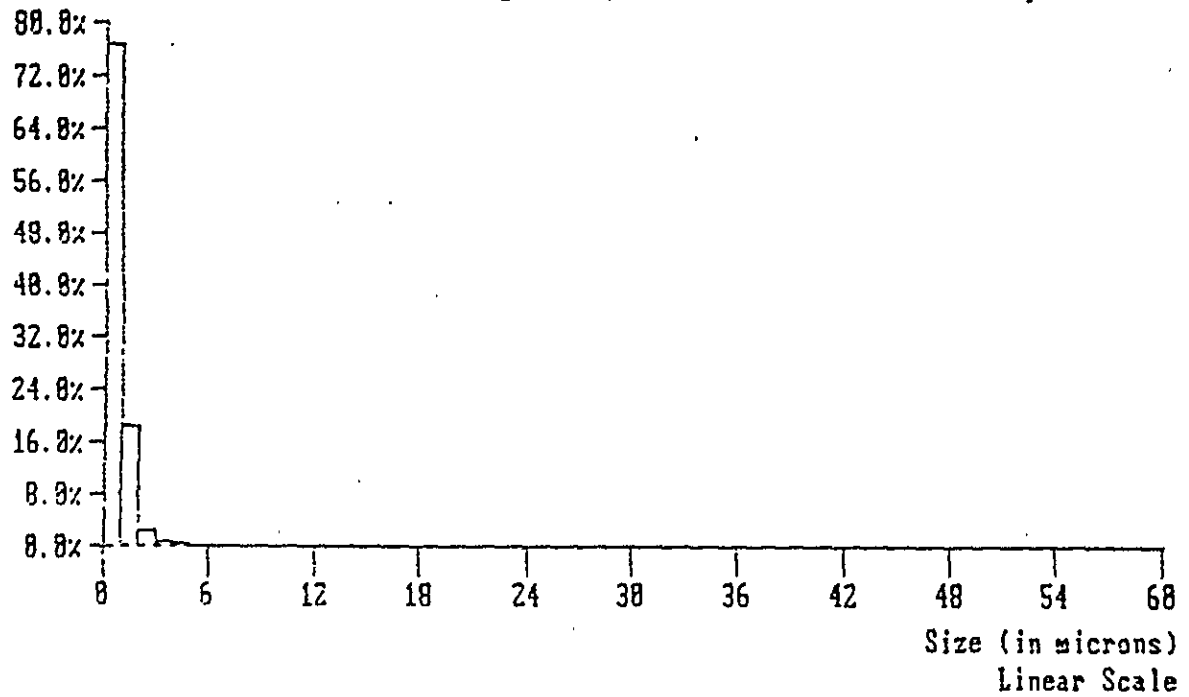


Figure 5-12b. Core 31, Segment 7, Particle Size: Volume Density.

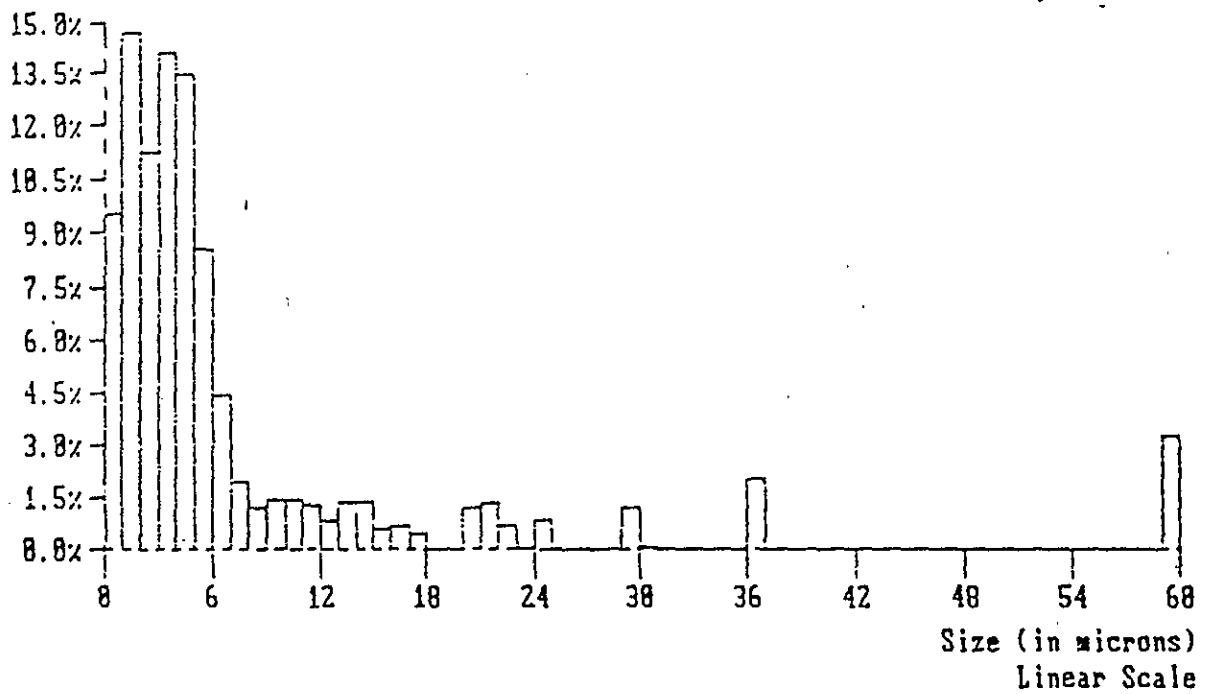


Figure 5-13a. Core 31, Segment 8, Particle Size: Number Density.

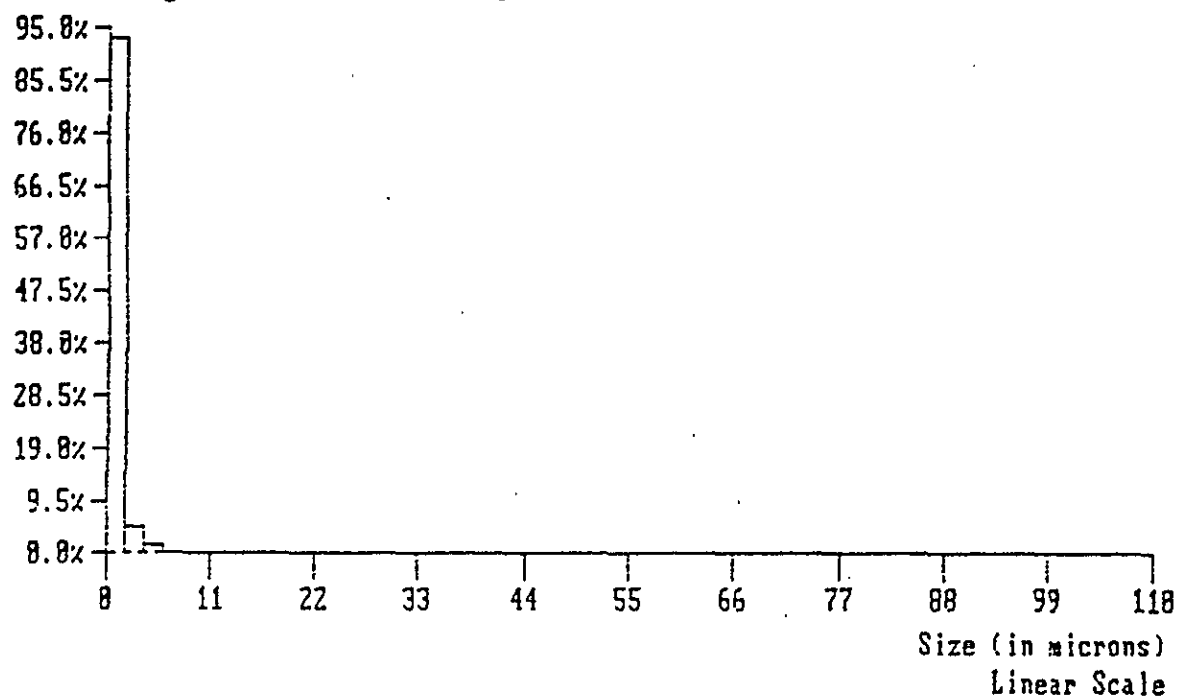


Figure 5-13b. Core 31, Segment 8, Particle Size: Volume Density.

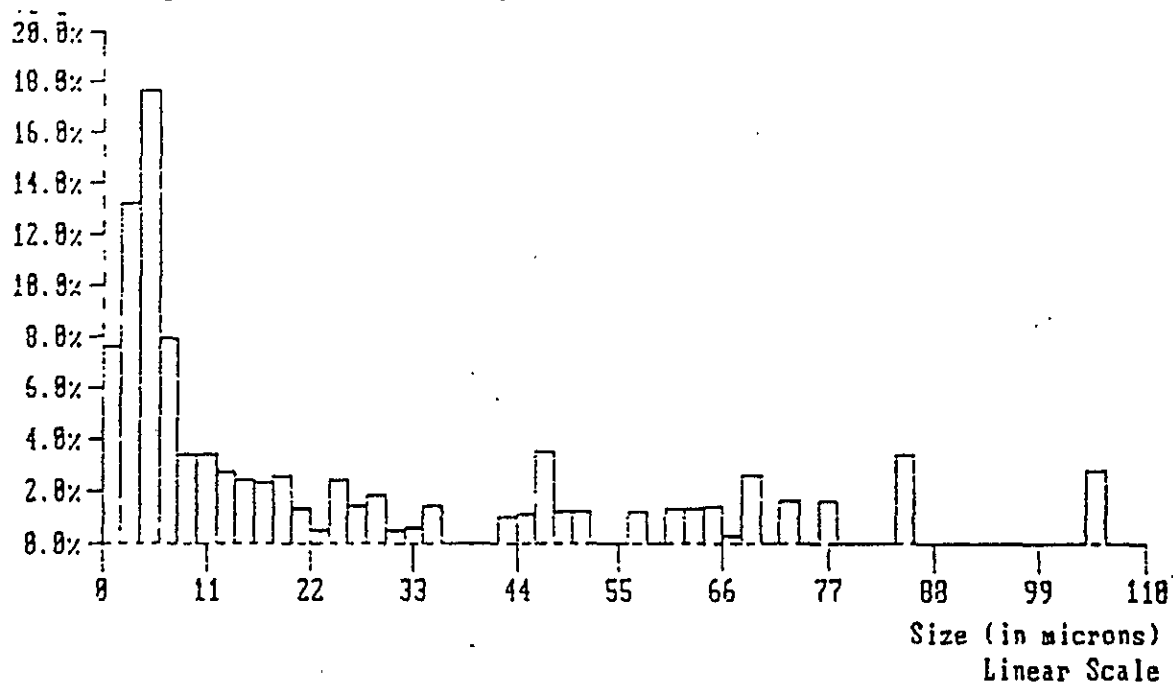


Figure 5-14a. Core 31, Segment 9, Particle Size: Number Density.

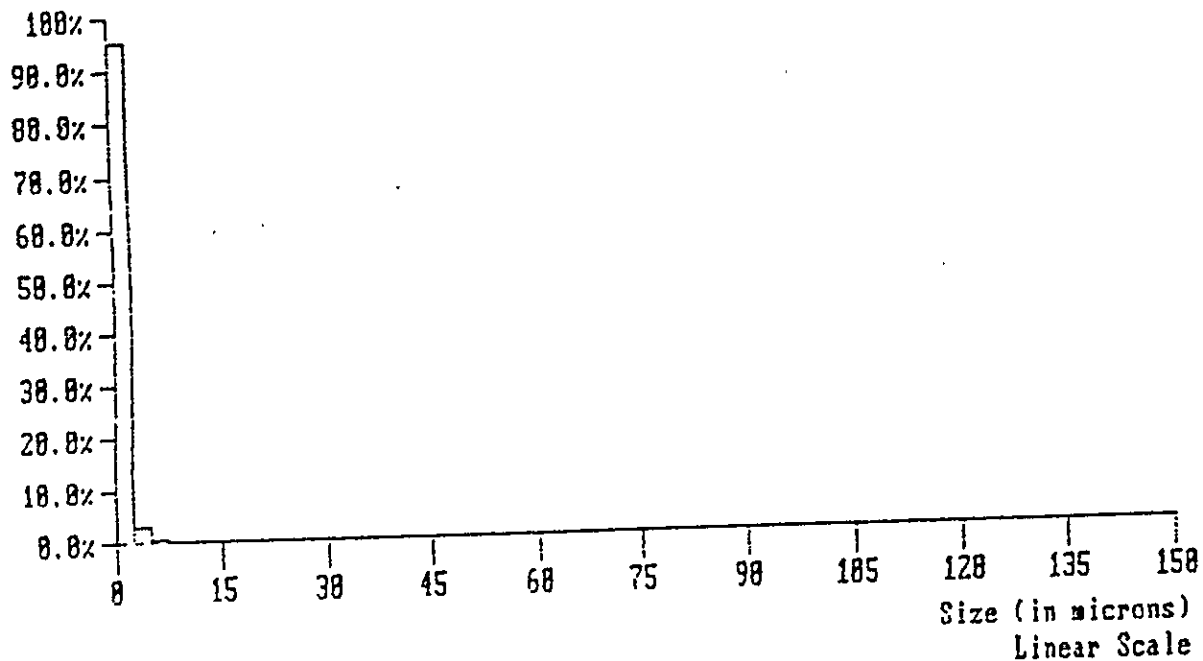


Figure 5-14b. Core 31, Segment 9, Particle Size: Volume Density.

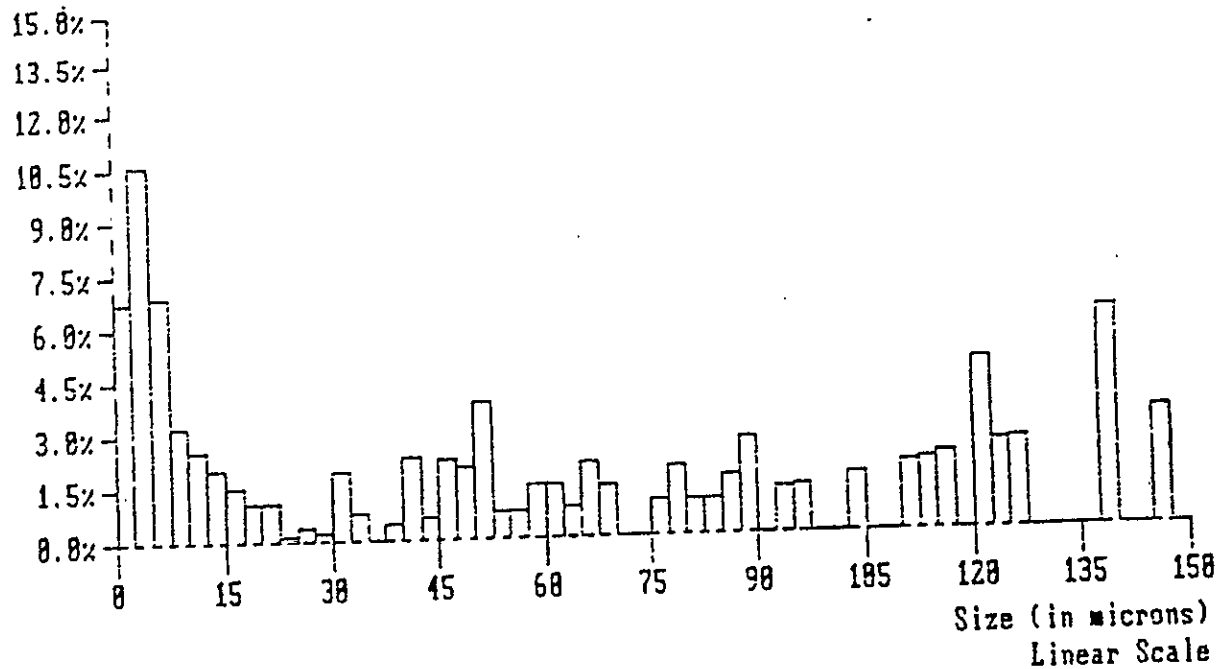


Table 5-15. Grab Sample Physical Properties Summary.

Property	Grab sample #1	Grab sample #2	Grab sample #3	Average value
Specific gravity	1.036	1.038	1.033	1.036
pH	11.57	11.59	11.78	11.65
Wt% H ₂ O	92.70	92.90	92.90	92.83
Wt% H ₂ O (TGA)	91.17	91.73	90.24	91.05
Settled solids (vol %)	< 1%	< 1%	< 1%	< 1%

The grab samples were clear yellow liquids with no particulate.

Table 5-16. Physical Properties Summary.

Property		Sample	
		Core 31, segment 2	Core 31, segment 8
Settled solids (vol%)	As-Received	100%	100%
Wt% Solids		22.4	29.3
Wt% Undissolved solids		19.0	25.4
Density (g/mL)		1.19	1.28
Centrifuged samples			
Vol%	1 hour at 1,000 gravities	65.8	71.9
Wt%		67.3	75.9
Centrifuged supernate density (g/mL)		1.07	1.10
Centrifuged solid density (g/mL)		1.22	1.34

The 1 to 1 dilution for segment 8 reaches a final volume-percent settled solids of about 80 percent (see Figure 5-17a). Settling is observed throughout the three-day period, but the majority of the settling is observed in the first 10 hours. The 3 to 1 dilution reaches a final volume-percent settled solids of approximately 40 percent. Again, settling is observed over three days and the first 10 hours is when the majority of the solids settle. Qualitatively, the settling behavior for both sample dilutions is a shallow, nearly linear relationship between the initial fluidization of the material and the first 10 hours of settling. The slope of this line is much more gradual than that of segment 2 for the corresponding dilutions. After the first 10 hours, the final 15 percent of the suspended solids take up almost the rest of the time settling in a long, gradual decline before coming to equilibrium. Table 5-17 summarizes the settling behavior for the samples investigated. Figures 5-15a through 5-17b illustrate the setting behavior over time.

Table 5-17. Settling Comparison for 1 to 1 and 3 to 1 dilutions for Core 31 Segments 2, 4, and 8.

Analyte	Segment 2		Segment 4		Segment 8	
Dilution: water to sample	1:1	3:1	1:1	3:1	1:1	3:1
Final volume % solids	87	52	22	22	80	40

5.4 ANALYTICAL RESULTS--ENERGETICS

TGA and DSC were performed on subsegment and core-composite material from tank 241-T-111. These two thermal analysis techniques are used to determine the thermal stability or reactivity of a material. In DSC analysis, heat flow over and above the usual heat capacity of the substance is measured while the substance is exposed to a linear increase in temperature, i.e., the change in temperature, divided by the time elapsed is constant ($dT/dt = \text{constant}$). While the substance is being heated, a cover gas (usually air or N_2) is passed over the waste material to remove any gases being released. The onset temperature for an endothermic or exothermic event on a DSC is determined graphically. The endpoints of the event are determined and a line is drawn between them to establish a base. A line tangent to the initial side of the event is drawn until it intersects the base. From that point of intersection, a vertical line is constructed to the temperature scale at the bottom of the DSC curve. That temperature is the onset temperature of the event.

TGA measures the mass of a sample while the temperature of the sample is increased at a constant rate. The X-axis is representative of the running time of the analysis as well as the temperature increase of the sample during analysis. The Y-axis represents the weight percent of the sample and is effectively unitless. As with the DSC, a cover gas is passed over the sample during heating. Any decrease in the weight percent of the sample represents a loss of gaseous matter from the sample either through evaporation or a reaction that forms gas phase products.

DSC is often used to measure thermal decomposition temperatures, heats of reaction, reaction temperatures, melting points, and solid-solid transition temperatures. TGA is used to measure thermal decomposition temperatures, water content, and reaction temperatures. The two methods often provide complementary information.

Figure 5-15a. Settling Rate Data for Tank 241-T-111 Core 31, Segment 2, 1 to 1 Dilution.

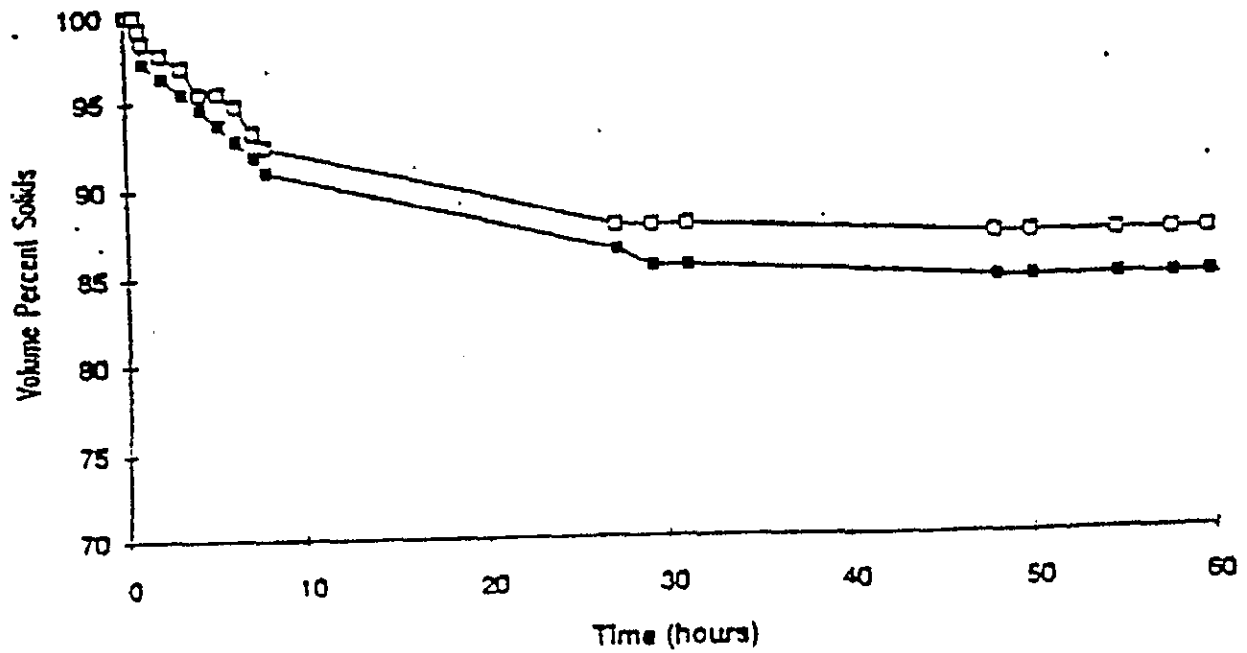


Figure 5-15b. Settling Rate Data for Tank 241-T-111 Core 31, Segment 2, 3 to 1 Dilution.

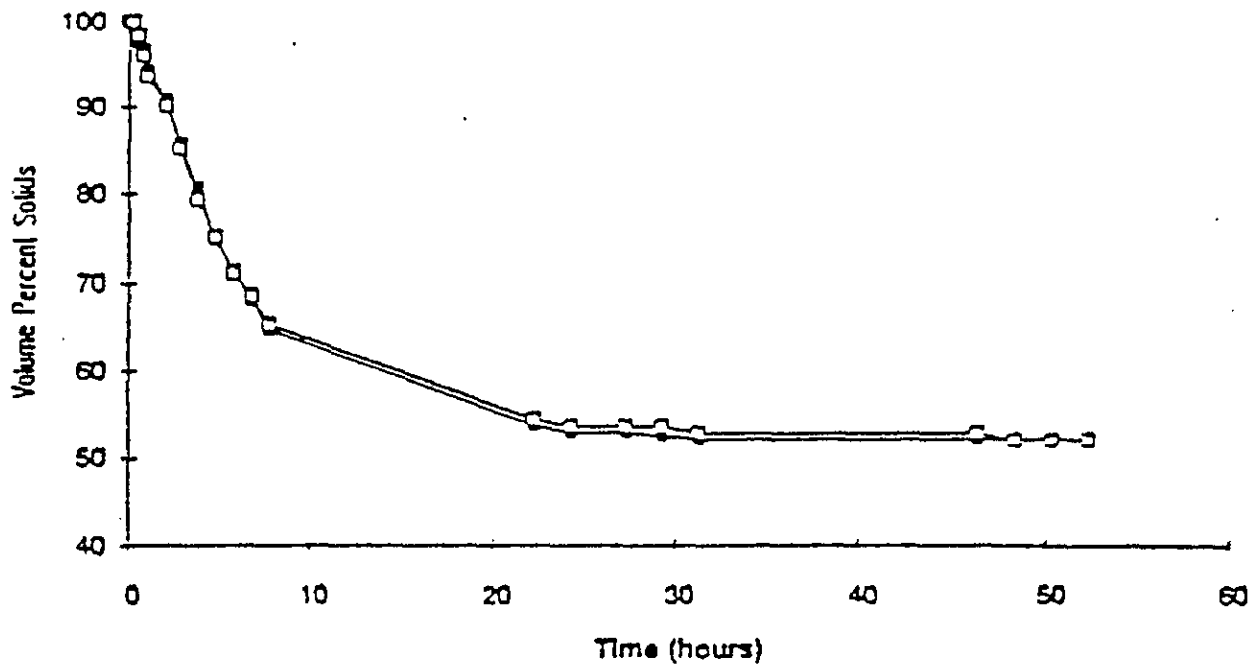


Figure 5-16a. Settling Rate Data for Tank 241-T-111 Core 31, Segment 4, 1 to 1 Dilution.

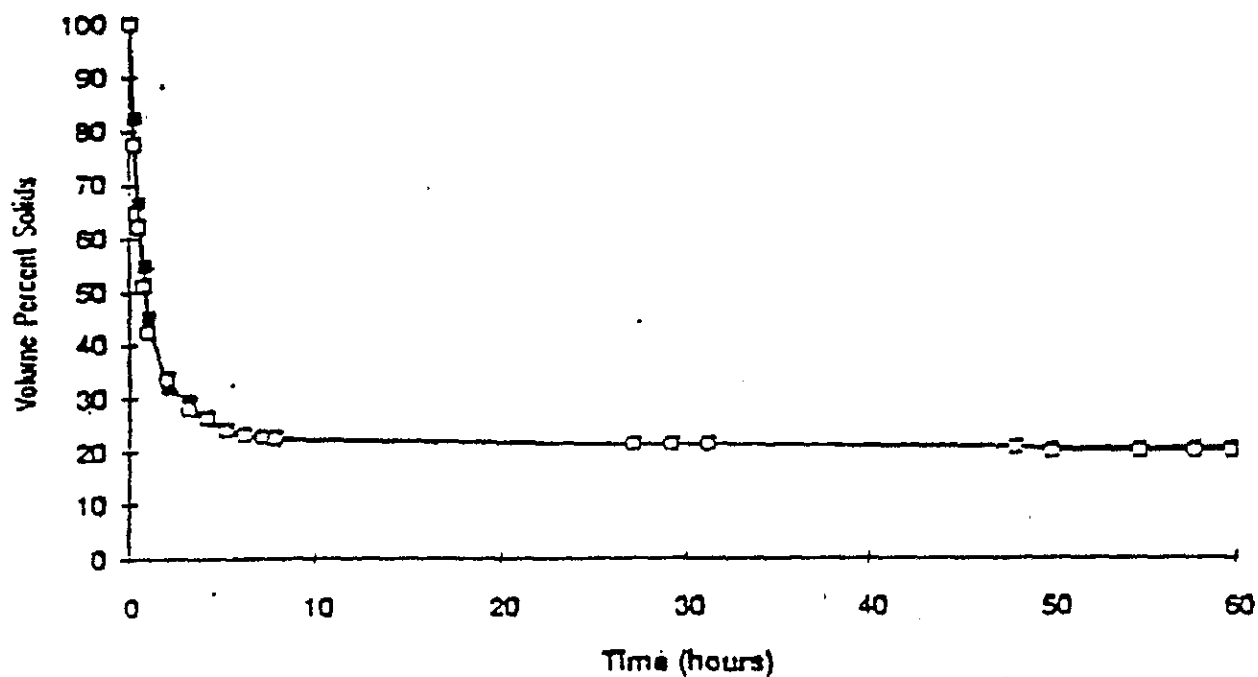


Figure 5-16b. Settling Rate Data for Tank 241-T-111 Core 31, Segment 4, 3 to 1 Dilution.

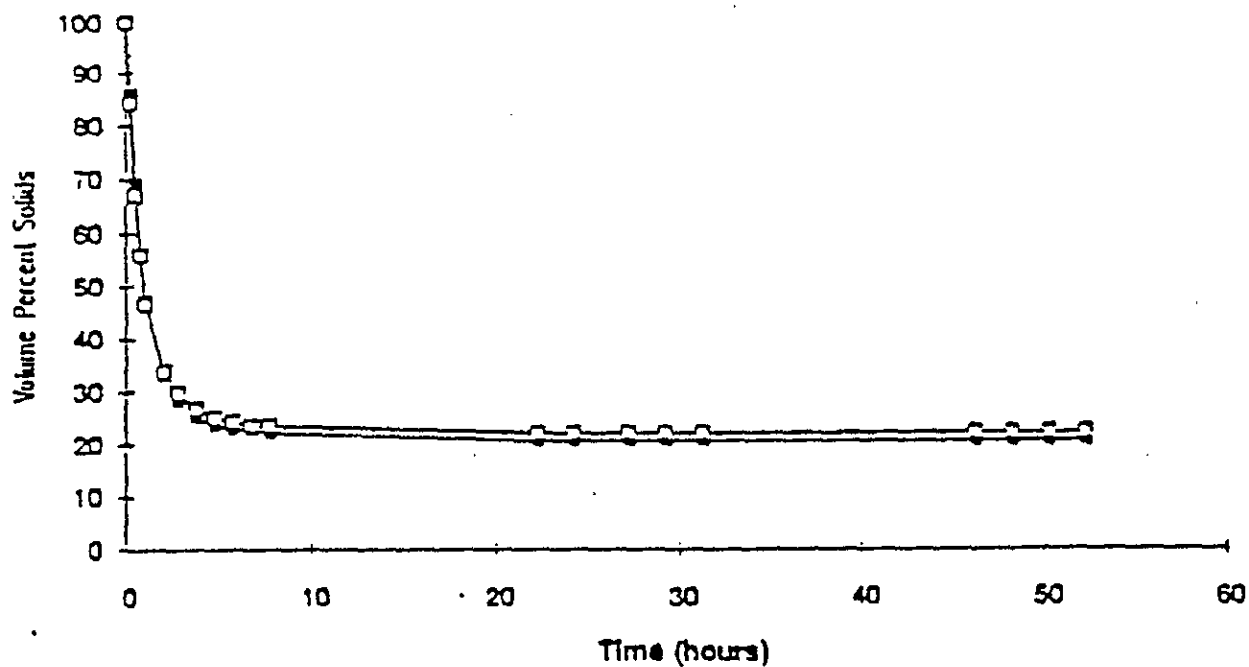


Figure 5-17a. Settling Rate Data for Tank 241-T-111 Core 31, Segment 8, 1 to 1 Dilution.

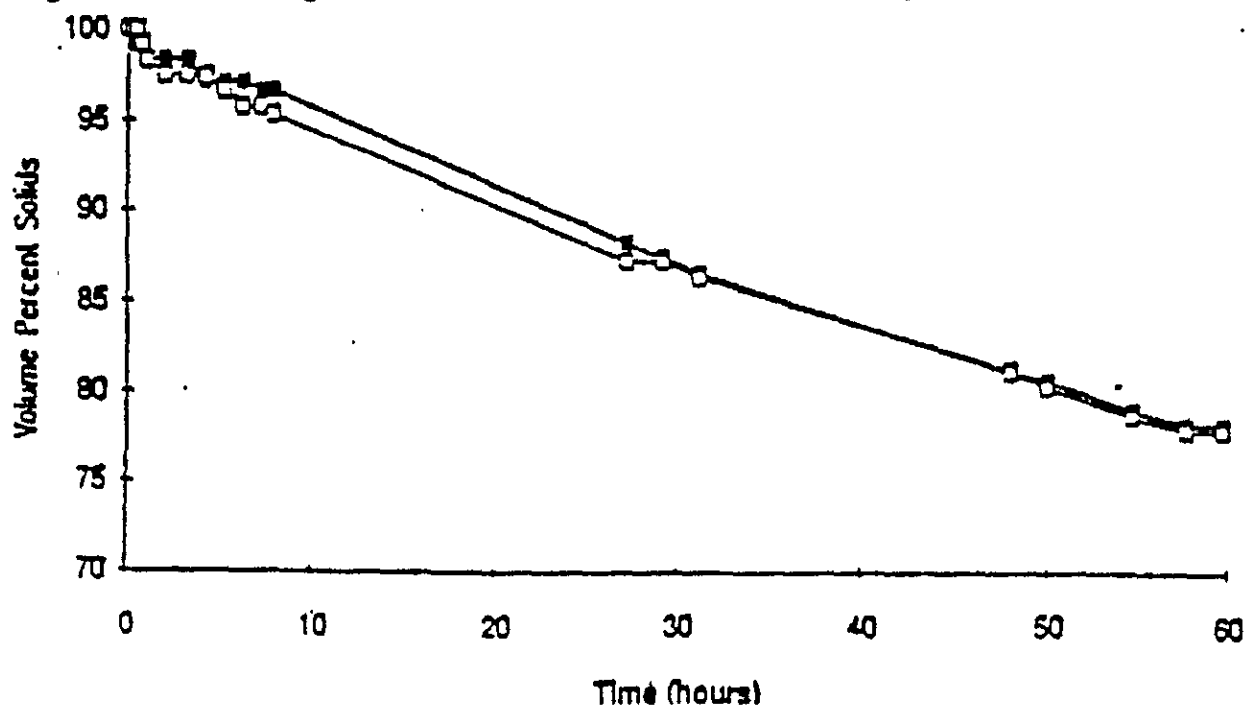
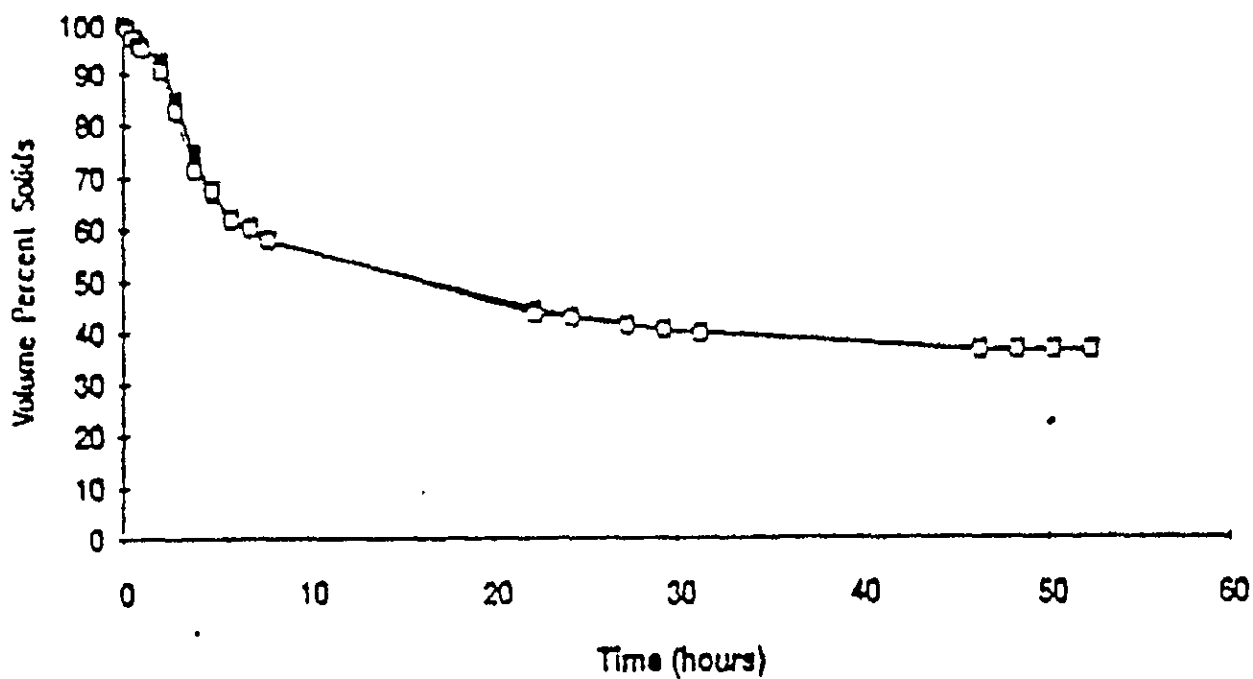


Figure 5-17b. Settling Rate Data for Tank 241-T-111 Core 31, Segment 8, 3 to 1 Dilution.



5.4.1 Remarks on the Interpretation of Differential Scanning Calorimetry/Thermogravimetric Analysis Data

Tables 5-18, 5-19, and 5-20 summarize the results of the thermal analyses performed. Although DSC assays were performed on the grab samples, the results were uniformly negative (i.e. no exotherms were observed). Where exotherms were observed, there are two significant features seen on the DSC and one on the TGA plots. The endothermic DSC event overlaps the area where the substantial majority of the sample mass is lost as recorded by the TGA, suggesting that this endotherm is a result of the evaporation of water from the sample. The values presented in the tables may not exactly match the values derived from the DSC and TGA plots, especially exotherm magnitudes. This is because interpreting these semi-quantitative analyses requires considerable experience and judgement on the part of the analyst, and differences in perception and judgement between readers can be expected in a semi-quantitative analysis. McKinney et al. (1993), contains copies of all of the DSC and TGA traces and results.

Additional physical properties work was performed to expand the understanding of the exothermic behavior of some of the segments (WHC 1994, Delegard 1994). Table 5-21 presents additional energetics results for core 33, segments 1 and 2. These samples were dried under a vacuum at 60 °C before analysis, using either air or nitrogen as a cover gas. Even after drying, the samples retained 10 to 12 weight percent water. Table 5-22 presents a brief summary of the analytical results for the average sample properties as-received after centrifuging samples from core 31, segments 3 and 7, and core 33, segments 1 and 7, at 500 gravities for 113 hours.

5.4.2 General Comments on the Differential Scanning Calorimetry/Thermogravimetric Analysis Behavior of the Samples

The first transition in each sample is endothermic, begins at the lower temperature limit of the analysis (30 °C), and essentially is complete between 140 and 180 °C. The most likely phenomenon occurring in this region is the release of the bulk and interstitial water in the core sample material. The endotherms exhibited in this region are substantial (typically in excess of 1,000 J/g). These values are per gram of wet sample. If divided by the mass fraction lost during analysis, they range from 1,600 to 1,900 J/g (dry) and correspond roughly with the heat of vaporization of water (2,260 J/g). The TGA water content corresponds reasonably well with the water loss observed in a gravimetric weight percent solids determination; however, the gravimetric weight percent water assay is consistently lower.

Table 5-18. Percent Water Analyses Results from Tank 241-T-111.

Sample I.D.	Core 31 average gravimetric Wt% loss	Core 31 average TGA transition 1 Wt% loss	Core 33 average gravimetric Wt% loss	Core 33 average TGA transition 1 Wt% loss
Segment 1	80.3	87.0	80.4	NM
Segment 2	82.4	87.0	85.7	80.6
Segment 3	86.0	85.0	81.8	88.5
Segment 4	77.3	82.8	79.9	89.5
Segment 5	80.9	88.0	78.2	88.8
Segment 6	No sample	No sample	75.8	84.4
Segment 7	76.8	84.8	71.7	85.8
Segment 8	76.6	85.6	75.4	84.8
Segment 9	75.8	71.0	76.0	85.2
Segment 9B	70.4	72.1	NA	NA
Composite 1	74.6	73.3	76.5	81.6
Composite 2	75.9	70.2	77.1	80.8

Table 5-19. Differential Scanning Calorimetry Energetics Results from Tank 241-T-111, Core 31 (wet basis).

Core sample 31	Transition 1			Transition 2		
	Range (°C)	Avg. onset (°C)	ΔH range (J/g)	Range (°C)	Avg. onset (°C)	ΔH range (J/g)
Segment 1	43 - 141	43	1,088 to 1,406	200 - 387	200	-259 to -273
Segment 2	46 - 149	46	1,108 to 1,643	200 - 398	225	-256 to -264
Segment 3	45 - 160	50	1,210 to 1,233	195 - 405	198	-263 to -448
Segment 4	44 - 165	44	1,235	200 - 390	200	-55.7
Segment 5	NR	--	Endotherm NR	NA	NA	No Exotherm
Segment 6	NA	--	---	---	--	NA
Segment 7	50 - 164	50	1,488	165 - 400	NA	No Exotherm
Segment 8	50 - 153	50	1,534	154 - 400	NA	No Exotherm
Segment 9	61 - 158	61	1,437	159 - 400	NA	No Exotherm
Composite 1	NR	--	Endotherm NR	256 - 339	257	-23.6 to -37.0
Composite 2	NR	--	Endotherm NR	260 - 334	262	-18.5 to -22.9

NOTE: To convert from J to cal, divide by 4.18.

NOTE: Negative ΔH indicates an exotherm.

NA = Not applicable

NR = Not resolved.

Table 5-20. Differential Scanning Calorimetry Energetics Results from Tank 241-T-111, Core 33 (wet basis).

Core Sample	Transition 1			Transition 2		
	Range (°C)	Avg. onset (°C)	ΔH range (J/g)	Range (°C)	Avg. onset (°C)	ΔH range (J/g)
Segment 1	49 - 168	49	958 to 1,604	168 - 374	184	-218 to -293
Segment 2	45 - 179	50	1,346 to 1,496	168 - 438	174	-454 to -645
Segment 3	NA	--	Endotherm NR	237 - 400	237	-49.3
Segment 4	NA	--	Endotherm NR	NA	--	No Exotherm
Segment 5	NA	--	Endotherm NR	NA	--	No Exotherm
Segment 6	NA	--	Endotherm NR	NA	--	No Exotherm
Segment 7	NA	--	Endotherm NR	NA	--	No Exotherm
Segment 8	NA	--	Endotherm NR	NA	--	No Exotherm
Segment 9	NA	--	Endotherm NR	NA	--	No Exotherm
Composite 1	NA	--	Endotherm NR	NA	--	No Exotherm
Composite 2	NA	--	Endotherm NR	NA	--	No Exotherm

NOTE: To convert from J to cal, divide by 4.18.

NOTE: Negative ΔH indicates an exotherm.

NA = Not applicable.

NR = Not resolved.

Table 5-21. Differential Scanning Calorimetry Energetics Results from Tank 241-T-111, Core 33 (dry basis).

Laboratory-core sample-air/N ₂	Transition 1			Transition 2		
	Range (°C)	Avg. onset (°C)	ΔH range (J/g)	Range (°C)	Avg. onset (°C)	ΔH range (J/g)
222-S core 33, seg. 1, Air	---	---	NR--Dried	158 - 405	NR	-1,857 to -1,882
222-S core 33, seg. 2, Air	---	---	NR--Dried	130 - 425	NR	-251 to -269
222-S core 33, seg. 2, N ₂	---	---	NR--Dried	130 - 430	NR	-288 to -309
222-S core 33, seg. 2, N ₂	---	---	NR--Dried	128 - 418	NR	-180 to -187
222-S core 33, seg. 2, N ₂	---	---	NR--Dried	123 - 421	NR	-163 to -175
222-S core 33, seg. 2, N ₂	---	---	NR--Dried	121 - 438	NR	-336
325 core 33, seg. 2, N ₂	---	---	NR--Dried	107 - 394	199	-836 to -898

NOTE: To convert from J to cal, divide by 4.18.

NOTE: Negative ΔH indicates an exotherm.

NA = Not applicable

NR = Not resolved.

Table 5-22. Additional Segment-level Physical Properties Measurements (1994).

Analyte	Core 31, segment 3		Core 31, segment 7		Core 33, segment 1		Core 33, segment 7	
	As-received	Centrifuged	As-received	Centrifuged	As-received	Centrifuged	As-received	Centrifuged
Gravimetric water (%)	79.53	64.96	74.72	62.06	79.56	65.49	74.07	59.95
TGA (%)	76.72	55.36	74.06	55.83	78.08	51.37	78.1	45.15
Density (g/mL)	1.24	1.09	1.19	1.20	1.16	1.19	1.20	1.29
ΔH exotherm range (J/g)	-112 to -191	-465.3 to -546.9	-10.2 to -33.1	0	-249 to -254	-822.4 to -838.1	-37.5 to -41.4	0

When there is a second transition it is usually substantial and the energetic behavior is readily quantifiable in all of the samples analyzed where exotherms are observed. Any weight loss in the second transition region (generally temperatures above 200 °C) was not readily quantifiable, whether exotherms were observed or not. The results for the samples from segments 1, 2, and 3, which are from the upper portion of the tank, indicate significant differences in thermal behavior compared to other samples from deeper in the tank, further suggesting a difference in waste type. In addition, because of the observed exothermic behavior for the top 3 segments from cores 31 and 33 and the results from Baldwin (1994), the present TOC assay is not considered capable of measuring the TOC in the waste. Resolution of the actual magnitude of the exotherm, its reaction mechanism, and speciation of the fuel is still continuing.

5.5 OVERALL ANALYTICAL DATA SUMMARY

Several characterization and safety issues are defined by certain bulk amounts or weight percent of a given analyte. Table 5-23 presents the nominal concentration and calculated bulk amounts of the analytes in the waste matrix. The gross waste inventory in the tank is estimated to be 2,171,000 kg wet solid. It is assumed that by the publication of this report, no drainable liquid will remain in the tank. Simpson (1994, Appendix C) presents the data, assumptions, and calculations used to determine the following values.

Table 5-23. Overall Data Summary and Inventory Estimates. (3 pages)

GROUP	Process history ¹ (Agnew 1994)	TRAC (Jungfleisch 1984)	Analytical data range (most quantitative assay)	1992 cores 31 and 33 average	Tank inventory based on 1992 core data
CATIONS	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	kgs
Be.f	---	---	< DL	< DL	< 0.22
B.a	---	---	23.4 - 32.2	28	60.8
Na.f	74,200	0	33,900 - 39,800	37,000	80,300
Mg.a	---	---	290 - 479	377	820
Al.f	0	0	459 - 693	570	1,240
Si.f	2,800	0	5,410 - 5,960	5,670	12,300
P.f	(as PO_4^{3-})	(as PO_4^{3-})	9,070 - 11,600	10,400	22,600
S.f	(as SO_4^{2-})	(as SO_4^{2-})	1,080 - 1,350	1,230	2,660
K.a	3,700	0	1,020 - 1,210	1,140	2,460
Ca.f	0	0	2,050 - 2,760	2,420	5,260
Ti.f	---	---	22.3 - 72.9	48	104
V.f	---	---	12.1 - 16.5	14.5	31.5
Cr.a	33	719	1,840 - 2,140	1,980	4,290
Mn.a	90	507	6,140 - 6,710	6,330	13,700
Fe.f	9,400	10,300	15,900 - 20,500	18,500	40,200
Ni.a	0	0	108 - 151	132	285
Co.f	---	---	10.1 - 13.3	4.5	9
Cu.f	---	---	22.1 - 36.3	29.3	63
Zn.f	---	---	104 - 110	106	231
As.a	---	---	< DL	< 3.3	< 7.2
Se.a	---	---	< DL	< 1.5	< 3.3
Sr.f	0	---	280 - 334	300	651
Zr.f	0	0	4	NR	---
Ag.f	---	0	37.1 - 221	130	278
Cd.f	---	---	6.42 - 10.7	5.8	12.6
Sn.a	---	---	1.61 - 4.21	2.5	5.4
Sb.a	---	---	22.6 - 36.5	31.4	70
Ba.a	---	0	57.0 - 87.3	69	150
La.a	12,700	512	3,620 - 4,890	4,220	9,160
Ce.a	0	0	28.6 - 37.8	33.7	73.2
Hg.CVAA	---	---	1.08 - 1.83	1.43	3.1
Pb.f	0	0	267 - 484	365	792
Bi.a	23,200	963,000	23,300 - 28,500	26,000	56,300
U.LF	140	---	1,950 - 5,200	3,550	7,700

Table 5-23. Overall Data Summary and Inventory Estimates. (3 pages)

GROUP	Process history ¹ (Agnew 1994)	TRAC (Jungfleisch 1984)	Analytical data range (most quantitative assay)	1992 cores 31 and 33 average	Tank inventory based on 1992 core data
RADIONUCLIDES					
Analyte	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	Ci
Total Alpha	---	---	0.166 - 0.649	0.368	NA
Total Beta	---	---	8.83 - 21.5	15.1	NA
²⁴¹ Am	---	0.0092	0.0382 - 0.0478	0.0425	92.4
^{239/240} Pu	0.009	0.055	0.134 - 0.628	0.304	660
¹³⁷ Cs	0.086	0	0.103 - 0.237	0.166	360
⁹⁹ Tc	---	0	0.00473 - 0.0114	0.0079	17.2
⁵⁹ Ni	---	---	3.35E-05 - 9.4E-05	5.04E-05	0.11
⁶³ Ni	---	---	0.0036 - 0.011	0.0057	12.4
⁹⁰ Sr	0.176	1.84	3.43 - 7.43	5.41	11,800
¹⁴ C	---	0	< DL	< DL	---
³ H	---	---	< DL	< DL	---
ANIONS					
Analyte	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	kgs
OH ⁻	8,900	15,700	3,300 - 6,000 ²	---	---
NH ₃	---	---	< DL	< DL	---
F ⁻	24,600	0	1,370 - 3,130	2,300	4,990
Cl ⁻	0	0	400 - 500	450	977
NO ₂ ⁻	0	0	525 - 952	793	1,720
NO ₃ ⁻	51,600	0	36,900 - 44,300	41,300	89,660
CO ₃ ⁻	0	0	as TIC	812	1,760
Total PO ₄ ⁻³	35,400	438,000	27,800 - 35,500	31,900	70,100
SO ₄ ⁻²	1,450	0	3,290 - 3,690	3,680	7,990
CARBON-BEARING SPECIES					
Analyte	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	Kgs
TOC	2,000	---	2,000 - 3,990	3,120	6,770
TIC	---	0	650 - 950	812	1,760
C ₂ H ₃ O ₂ ⁻	0	0	NM	---	---
C ₂ O ₄ ⁻²	7,200	---	NM	---	---
C ₆ H ₅ O ₇ ⁻	0	0	NM	---	---
Fe(CN) ₆ ⁻⁴	0	0	NM	---	---
EDTA	0	0	NM	---	---
HEDTA	0	0	NM	---	---

Table 5-23. Overall Data Summary and Inventory Estimates. (3 pages)

GROUP	Process history ¹ (Agnew 1994)	TRAC (Jungfleisch 1984)	Analytical data range (most quantitative assay)	1992 cores 31 and 33 average	Tank inventory based on 1992 core data
PHYSICAL PROPERTIES					
Wt% Water (Grav.)	72.5%	---	74.6 - 77.1	76.0%	1.65E+06 kg
Wt% Water (TGA)	72.5%	---	70.2 - 81.6	76.5%	1.66E+06 kg
Bulk Density (g/cm ³)	1.21	1.8	1.19 - 1.28	1.24	---
Supernatant Density (g/cm ³)	1.058	---	1.033 - 1.038	1.036	---

¹Process history estimates are determined using a simple linear combination based on the proportions of 2C and 224 waste contributed.

²OH⁻ is estimated from mass and charge imbalance.

6.0 INTERPRETATION OF ANALYTICAL RESULTS

Tank 241-T-111 had a relatively straightforward process history as documented in the transfer records. It received very few major types of waste that were likely to deposit solids during its operating history. The waste types, in chronological order, were as follows:

- 2C waste
- 224 Waste
- Decontamination streams from T Plant (221-T).

The purpose of this section is to attempt to identify and reconcile the location of the tank waste solids, thereby estimate the tank inventory for various analytes of importance.

The waste profile was identified by examining the available segment level assays for analytes or characteristics distinct to the waste types that were disposed in the tank, and then combining that information with what is known regarding the tank's process history. The first waste placed in the tank through the cascade inlet from tank 241-T-110 was 2C waste. Study of the process stream compositions indicates that this waste would be comparatively high in bismuth and phosphate in addition to the ubiquitous sodium, nitrate, and iron found in nearly all waste types. Elevated levels of fluoride, chromium, and sulfate are also expected. Qualitatively, the waste has been observed to be a gelatinous material. Anecdotal reports during this time also indicate that the cascade lines may have clogged in tank 241-T-111 and in other tank cascades receiving this type of waste. The 2C solids volume was measured to be between 723,000 L (191,000 gal) and 931,000 (246,000 gal) in 1953 (Anderson 1990).

The tank then received 224 waste. The solids from this waste are high in manganese, lanthanum, and fluoride, however, the 224 waste may have been combined with the 2C waste before being discharged to the tank. The estimated solids volume contribution for this waste type in tank 241-T-111 at the end of bismuth phosphate production in T Plant was between 594,000 and 802,000 L (157,000 and 212,000 gal).

The last major waste type disposed in the tank was T Plant decontamination waste. Much of the physical and chemical composition of this waste is unknown because it was a catch-all, consisting of various process residues, unused stock solutions, and aqueous decontamination solutions that contained surfactants (such as Turco*). Few predictions can be made from studying the historical process flowsheets in this case. Lack of analytical data and/or transfer records with regard to T Plant effluents later in tank 241-T-111's service life are a great source of uncertainty regarding the waste near the surface. One observation is that slightly higher TOC values may be anticipated near the surface because of the use of detergents in the decontamination waste stream and its chronological discharge sequence with respect to the other wastes. This waste stream is estimated to occupy the top segment of waste, or 198,000 L (53,000 gal). The sum of the wastes would range between 1.52 million L and

*Turco is a registered trademark of Turco Products, Inc.

1.93 million L (401,000 gal and 511,000 gallons), well within the reported range described in Anderson (1990). This waste volume would measure between 389.4 to 491.0 cm (153.3 to 193.3 in.), measured from the centerline and distributed evenly across the tank. The present surveillance level status is almost exactly in the middle of this range 1.73 million L (456,000 gal) and $440.2 \text{ cm} \pm 1.3 \text{ cm}$ ($173.3 \pm 0.5 \text{ in.}$) (Rios 1994).

Two common characteristics of all these waste types are high water content and relatively low activity. None of the waste streams disposed in this tank were concentrated through the evaporator; therefore, the waste tank would not have any salt cake. The uranium, plutonium, and fission product content of these wastes are uniformly low.

6.1 Review of the Analyte Profiles

The following conclusions are drawn from review of the available composite and segment analyses presented in Section 5, and the historical information presented in Section 2.

Core 31

The chemical analyses of core 31 indicate there are at least two primary types of material in distinct layers in the tank. The DSC traces for segments 1, 2, and 3 show exotherms far out of proportion to the measured organic content in the wastes. The temperature range where the wastes begin to show reactions are from 170 to 400 °C, but do not appear to be self-sustaining. Instead, the overall energy profile is highly endothermic, probably caused by the large amount of bound water (70 to 80 weight percent) that is evaporated from the sample before a reaction is initiated. The overall physical and chemical properties of the waste in the tank roughly correspond to the expected behavior and composition of 2C waste, with large quantities of bismuth, iron, and phosphorous, and no exothermic behavior. But, there is a substantial contribution of manganese and lanthanum in the composites. However, these analytes can be found in 224 waste, and historical data indicates that 224 waste was added to tank 241-T-111 later in its service life. Therefore, the analytical and historical data correspond reasonably well, except for the anomalous energetic results. At this time, there is no adequate explanation for the observed exotherms in the upper segments of tank 241-T-111 waste.

Core 32

Every segment of core 32 was compromised during the sampling process in some fashion. When the sampler operated properly, liquids were the only material recovered from this core. However, the sampler valve failed repeatedly. Photographs taken before and after the sampling event reveal that there was a plastic bag in the vicinity of the sampling area before coring operations. After core sampling, the bag can not be seen. It is surmised that the sampling drill string was obstructed by the bag during core sampling operations, causing the corruption of the samples. All samples from core 32 were rendered unusable or categorized as non-representative. Therefore, no assays were performed and no analytical results are reported.

Core 33

The chemical analyses of core 33 indicate there probably are three primary types of material in distinct layers in the tank. The extremely high manganese values in the top first segment of the tank are attributed to a combination of T Plant decontamination waste (i.e., the result of a final process flush during the decontamination of T Plant) and 224-waste solids deposited late in the tank's service life. Proceeding deeper into the tank, beneath the first segment, the distribution of bismuth, manganese, lanthanum, and chromium in the composites and the analyte profiles from the homogenization results through segment 3 support the conclusion that this material is still 224 waste. Segment 3 itself is suspected to be a transition layer, containing the boundary between the 224 waste and the 2C waste, based on the exothermic behavior of the waste as a function of depth. The TOC analysis indicates moderate amounts of residual organics in the waste.

Cesium-137 concentrations between the core composites vary within a factor of two, and the variation in the ^{241}Am is less than 13 percent. But the change in concentration as a function of depth for each of these analytes is much more significant. Both analyte profiles show a decreasing trend as a function of depth in core 33. The ^{137}Cs concentration decreases by more than a factor of 30 over the depth of the tank, and ^{241}Am decreases by a factor of 10 through segment 7 before rebounding somewhat in segment 9. The ^{137}Cs and ^{241}Am concentrations as a function of depth in core 33 show profiles consistent with the wastes believed to be associated with the segments: low overall ^{137}Cs and ^{241}Am values. But the relative radionuclide concentrations for the suspected 224 and T Plant decontamination wastes are higher than the 2C wastes. The ^{90}Sr concentration is also low, and ^{90}Sr is similar to ^{137}Cs in the magnitude of the change in concentration and as a function of location for both cores. However, there are no high radionuclide values anywhere in the tank, and the tank temperature further confirms the tank's low radionuclide content.

Lanthanum and phosphate/phosphorus demonstrate an increasing concentration profile as a function of depth. Between segments 1 and 3 and 3 and 5 there is an abrupt change in the concentrations of calcium, chromium, manganese, bismuth, lanthanum, and phosphorous, although after segment 5, the analyte concentrations tend to plateau, mirroring the behavior of the radionuclides. In addition, the DSC traces for segments 1, 2, and 3 show exotherms far out of proportion to the measured organic content in the waste. The temperatures where the wastes begin to show reactions range from 170 to 400 °C, but these reactions do not appear to be self-sustaining. Instead, the overall energy release is highly endothermic, probably from the large amount of bound water that is evaporated from the sample before a reaction is initiated.

In conclusion, the physical and chemical properties of the waste in the bottom half of the tank correspond to the expected behavior and composition of 2C waste, and the upper half of the tank is suspected to be 224 waste with a high manganese layer located in segment 1. Therefore, the analytical and historical data correspond well with the historical fill pattern, except for the anomalous energetic results. Presently there is no adequate explanation for the observed exotherms in the upper segments of tank 241-T-111 waste.

6.1.1 Entrance, Exit, and Mixing Effects on Analyte Distribution

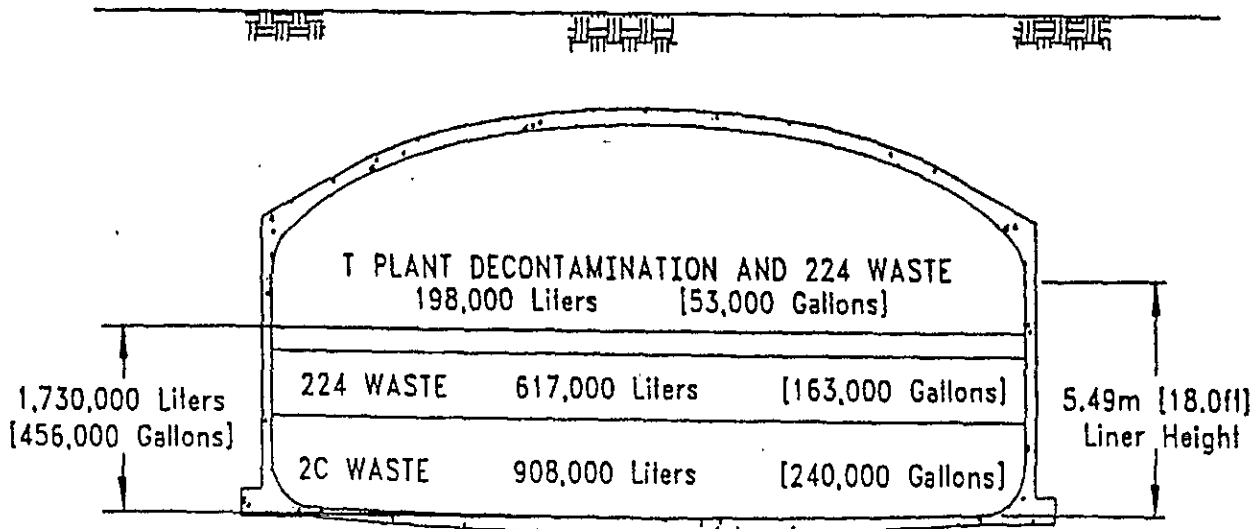
Figure 5-1 shows an elevation and plan view of where the core samples were taken. Important items to note are the arrangement and location of the risers and cascade lines (inlet and outlet). Their configuration can have a substantial impact on the distribution of waste in the tank, and observations with regard to sampling. However, the waste entrance and exit points for the tank over its service life are not well documented, therefore the spatial relationship and proximity to the sample risers is not known. The decant "float and flex" pump contained a 6.1-m (20-ft) section of flexible hose that could traverse a relatively wide area under and around the pumpout riser. The cascade fill line where 2C waste entered the tank is closer to the core 33 sample point than to the core 31 sample point. There was very limited discharge/transfer traffic from the other separations plants within T Farm or with the tank farms as a whole, so no highly enriched layer of radioactive material is expected to lie on top of the waste as has been observed in other tanks sampled. However, the relative concentration of radionuclides is observed to be higher in the upper portions of the tank.

As new wastes entered the tank and were distributed across it, the material under and around the tank pumpout could have been disturbed, and occasionally solids could have been transferred, in behavior similar to the last in, first out principle. It is believed that the material beneath the waste inlets, the cascades and perhaps a riser, would have been disturbed initially, but over time, large stratified layers resistant to mixing eventually would have built up. No deliberate mixing of the wastes was performed; therefore, where segment-level data is available, distinctions between waste types can be made. Some of the larger particulate materials discharged to the tank initially may have settled out near the inlet because they were not as flocculent or as easily suspended as some of the other solids. This settling behavior may have provided a slight degree of separation. Therefore, the influence of the waste inlet and outlet locations can provide insight to the analyte distribution and waste profiles between cores 31 and 33. These factors may account for the nominally observed lateral heterogeneity between cores 31 and 33; however, it must be noted that this lateral heterogeneity is very slight and there may be several other factors contributing to this observation.

6.1.2 Waste Profile

Given the historical and analytical data, it is possible to develop a rough representation of the wastes as they presently are configured in tank 241-T-111. Figure 6-1 shows a representation of the overall waste profile of tank 241-T-111 and the assumed volumes, boundaries, and positions of the various individual layers as they are believed to exist.

Figure 6-1. Waste Profile of Tank 241-T-111.



- Dished bottom and tank layer 1: 2C, 908,000 L (240,000 gal)
- Tank layer 2: 224 waste, 617,000 L (163,000 gal)
- Tank layer 3: T Plant decontamination and 224 wastes, 198,000 L (53,000 gal)

6.2 WASTE SUMMARY AND CONDITIONS

Historically, 241-T-111 was a non-watch list single-shell tank with no previous indication of a potential safety issues. All waste receipts were 2C waste, 224 waste, or residues from the T Plant cleanout. Flowsheet records indicate that small amounts of oxalate are present in 224 waste (at 0.028 M) (Schneider 1951). As a result of DSC measurements, tank 241-T-111 was added to the Organic Watch List on March 4, 1994 and further concerns have been raised about the tank's integrity.

When tank 241-T-111 was sampled, normal paraffin hydrocarbon was used as a hydrostatic fluid, presenting a potential contamination source and bias for the DSC. However, when taking the first segment, no normal paraffin hydrocarbon was used, and sample recovery for the other segments in the cores was excellent. No voids or separable liquid layer were observed on extrusion of the samples, and results from the gas chromatograph/mass spectrometer for normal paraffin hydrocarbons components showed only trace amounts, precluding significant sample contamination from the hydrostatic head fluid. Furthermore, experiments have demonstrated that normal paraffin hydrocarbons steam distill away before reaching the reaction temperatures observed in DSC assays of the samples. In the deeper segments and in the composites, core 31 demonstrates some activity, but not to the extent shown in the upper segments. In core 33, no significant exotherms are evident in the composite. The photographs of the extruded waste material demonstrated that the all of the core samples were viscous, gel-like materials with very little free liquid, and that they held

their shape relatively well. During the physical testing of the core 31, segment 2 solid sample, when the sample was centrifuged, there was some separation of free water from the gel. Later physical testing did show some separation of liquid from the waste matrix for segment 7, but again, no separable phase was observed in the liquid (Delegard 1994). In each case, the liquid did not appear to have any distinct layers, therefore no liquid organics are considered to contribute to this waste matrix. In addition, although historically there have been problems with both volatile and semi-volatile organics analysis methods and holding times on these samples, all of the results from these assays show levels of these compounds below EPA contract laboratory procedure quantitation limits.

This information, coupled with data from the organic vapor monitor taken during the recent liquid sample effort (Simpson 1994, Appendix C), supports the contention that there are no substantial liquid organics in the tank. The organic vapor monitor results from the vapor space of tank 241-T-111 show a reading of 9.2 parts per million over a three minute monitoring interval: a detectable concentration, but far below the established safety criterion of 20 percent of the lower flammability limit. This result from the organic vapor monitor is not unexpected because small quantities of ammonia were observed in the grab samples and historically ammonia was used as a process chemical in the tank wastes. Over time, the ammonia is believed to have dissipated slowly to the levels observed today. It is also believed that the vapor space of this tank is relatively homogenous, and therefore, large concentration gradients for organics and other materials in the vapor space are not plausible. Differences of 2 to 10 times are within the realm of possibility (10 times being an extreme). Factors higher than that are not considered credible. For comparison, the vapor space of tank 241-C-103, which has a known organic liquid layer, was found to be 200 parts per million. Furthermore, a simplified modeling scenario of tank 241-T-111 shows that if normal-paraffin-hydrocarbon-type liquid organics were present, they would be in much greater quantities than detected in the organic vapor monitor (Simpson 1994, Appendix C).

To conclude, the waste in tank 241-T-111 is a complex material, primarily made up of water and organic and inorganic salts in a gel-like matrix. The insoluble solids are a mixture of phosphates, silicates, hydrated oxides, and hydroxides in combination with calcium, chromium, lanthanum, iron, bismuth, manganese, and uranium. The soluble analytes are primarily sodium, nitrate, sulfate, and fluoride. Phosphorous is nearly evenly divided between its soluble and insoluble forms. Substantial exotherms were detected in segments 1, 2, and 3, with the reactivity tailing off in segment 4 of core 31 and in segments 1, and 2, with the reactivity tailing off in segment 3 of core 33. The exotherms were reported to be similar in size and temperature range. It is important to note that no exotherms are observed until the sample has been dried and heated to approximately 180 °C. The exotherms themselves do not appear to be kinetically fast, thus the reaction may not be able to sustain itself without being thermally driven, as they are in the DSC apparatus. The organics present appear to be in the form of slightly soluble salts, contributing to a gel or sol-like structure. This behavior would be consistent with the very high moisture content observed in these tanks and with the types of organics historically indicated to be in the waste: aqueous decontamination solutions using surfactants, not normal paraffin hydrocarbons or TBP-type organics. This would help explain their low volatility and reactivity, their presence in the solid phase, and their relative absence in the liquids. These materials are carbon-bearing and will, if given enough impetus in the form of a thermal driver, react; however, the reaction

does not appear rapid or self-sustaining, and will not occur without first removing the water from the gel. No other safety issue was found after critically reviewing the analytical, historical, and surveillance data.

Hypotheses Regarding Recent Behavior of 241-T-111

Recently, surveillance data indicated that there had been a relatively abrupt level change in tank 241-T-111 over the past 16 to 18 months. Approximately 2.5 cm (1 in.) of gradual sludge growth was observed over the last eight-year period, followed by an approximately 4.1-cm (1.6-in.) decrease in surface level over 16 months. This situation is cause for concern. Tank 241-T-111 is an assumed leaker, therefore there is the possibility that the tank has leaked again and waste is being lost to the environment. This is not an acceptable condition. *Tank Farm Operating Procedures* (Boyles 1992) specify that when a level drop in a tank is observed, the observation must be accompanied by certain actions, and that a leaking tank must be pumped to eliminate any remaining drainable liquid to prevent further environmental contamination. However, the observed level decrease was not large enough to trigger action past investigation under present guidelines (Boyles 1992), and it was not resolved that a leak was the only explanation for the observed behavior. In fact, there were observers who believed there was another safety issue requiring consideration involved. The final outcome of the review, however, was the decision to pump the liquid in the saltwell of tank 241-T-111 to tank 241-SY-102 (Jenkins and Engelman 1994). This section recaps some of the alternative explanations presented for the surveillance data and provides some of the strongest and weakest points of the arguments put forth:

- **Tank is a "Re-leaker".** Evidence supporting this point of view is strong and it is one of the most favored explanations for the observed level drop. Tank integrity was questionable for a long period of time, and the tank was declared a leaker in 1984. Corrosion of tank liner is also evident from in-tank photographs. However, the change in surface level could be a localized phenomenon and in-tank photographs and observations of the extruded core material indicate that the waste is viscous and cohesive. Substantial damage to the tank liner and shell would be necessary for the evacuation of over 11,000 L (3,000 gal) of material and this condition is not indicated.
- **Long Cycle Gas-Release Tank.** This proposition is more speculative, but warrants consideration. Cyclic, gas generating behavior previously has been observed in Hanford Site waste tanks. Specifically, tank 241-T-110, the cascade source for tank 241-T-111, is on the Gas-Generation Watch List. Viscous waste material, such as that observed in tank 241-T-111, also appears to be able to retain generated gases. However, overall tank information, specifically the analytical chemistry results, indicate tank conditions necessary for gas generation as currently understood (i.e., high radionuclide and complexant levels), do not exist.

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- **Intrinsic Waste Matrix Changes.** This explanation is even more tenuous than the previous one, but again, the present understanding of the high-level waste tank matrices is very limited, so it is within the realm of possibility. Composition and structure of the waste (small particles, high water content, high ionic strength solution, and possible organic surfactants), may be similar to an emulsion. Over time, the low-level radiolytic action and thermal cycling of the waste may break down the colloidal characteristics of the matrix. The breakdown may be uneven, and there may even be a slurry-growth phase before the separation of the emulsion and the loss of free water through pinhole corrosion. However, that same degree of uncertainty regarding the content and structure of the waste matrix makes this hypothesis highly speculative without much more characterization information than currently exists.

 - **Structural Subsidence of the Waste.** This particular condition may be a contributing factor to the observed behavior, since it is acknowledged that the overall configuration of the waste generally is not very well known (and that the surfaces of the waste beds can be highly irregular), however it is not considered the main cause. After disposal into the tank, irregularities in the waste bed may have formed. The shifting of the waste bed over time as a result of gravitational compression is potentially responsible for the sudden drop in waste level. However, this rationale does not adequately explain the observed increase in tank level without involving another agent (i.e., a slow tank intrusion). Also, further slumping of the waste was not observed in the recent in-tank photographs, and the waste surface was observed to be reasonably uniform.

 - **Other Possibilities or Combinations of the Preceding Agents.** There may be more than one mechanism involved in the observed behavior, such as a long-term slow intrusion coupled with a subsequent upset and relatively rapid loss of material, especially of liquid, because the matrix appears to be quite viscous. There are a limited number of measurements taken and their location is fixed; therefore, local irregularities may be exacerbated. In addition, measurement error and bias also are significant when considering the magnitude of the drop in comparison with the error band.

6.3 TWRS PROGRAM ELEMENT CHARACTERIZATION SYNOPSIS

This section provides selected results obtained from core sampling for some of the most pertinent analytes for the various Tank Waste Remediation System (TWRS) program elements, including vitrification, retrieval, pretreatment, and waste tank safety. Analytes of interest will be reported on a level of resolution commensurate with the available data and program direction. Watch-list tanks will have segment or subsegment level analyses reported, while non-watch-list tanks are analyzed on a core composite basis. Analytes of interest to multiple programs generally will be reported only in one section. Further detail can be found in the body of the report or in the data packages.

6.3.1 Retrieval Program Data Summary: Physical Properties

A major objective of the characterization program is to measure the physical properties of the waste to support waste retrieval technology development. The analytical methods to determine the physical properties of the waste as it actually exists in the tank require 50 to 100 g of unhomogenized sample. In some cases, the limited amount of sample recovered constrains the number of analyses that can be performed. At the time of the sampling and analysis of tank 241-T-111 waste, no data quality objective existed to define the scope of the analyses. However, several analytes that specifically relate to physical properties were determined to be of interest to the program and are summarized here. The physical characteristics of tank waste are required to develop design criteria for waste retrieval equipment, provide a basis for simulated waste development, and to provide a basis for validation of equipment testing using design criteria and simulated waste. Selected rheological and physical properties are presented in Table 6-1. Further information regarding these analytes can be found in Section 5.3.

Table 6-1. Retrieval Program.

Analyte	Data range
Specific gravity (g/mL)	
--solids	1.19 - 1.28
--liquids (grab sample)	1.036
Shear strength	5,000 \pm 2,300 dynes/cm ²
Viscosity (mPa•s)	
--1:1 dilution @ 29 °C	Less than 2 mPa•s (cP)
Settled solids (Vol %)	100%
Weight % solids	22.4 to 29.3
Weight % undissolved solids	19.0 to 25.4
Particle size (μ m)	
--number distribution	85% < 2 μ m
--volume distribution	70% < 24 μ m

6.3.2 Final Disposal Program Data Summary

Bulk Constituent Concentrations for Pretreatment

Programmatic decisions pertaining to the design of pretreatment and final disposal systems shall be based upon the average characteristics of the tank waste. Therefore, the majority of the laboratory analyses shall be conducted on representative core composites. However, as noted in other documentation (Bell 1993), segment, subsegment, and additional analyses will be performed when directed. The constituent concentrations and inventories shall be calculated by either treating the core samples as random samples and averaging the results, or by using a spatial model. The calculated values will include an estimated total quantity of each selected analyte and its corresponding confidence interval (CI) based upon analytical and

sampling variability. Again, no data quality objective existed to define the scope of the analyses at the time tank 241-T-111 was sampled and analyzed. However, several analytes relating specifically to the most significant chemical and radiological contributors and their solubility properties were determined to be of interest to the program and are summarized here. Chemical analytes of interest are presented in Table 6-2. Trace analytes and more comprehensive chemical and radiological characterization information can be found in Section 5.0.

Table 6-2. Concentrations and Solubility of Principal Waste Components.

Analyte	Tank average concentration water prep: ($\mu\text{g/g}$)	Tank average concentration fusion prep: ($\mu\text{g/g}$)	% Water soluble
Calcium	61.8	2,420	2.55
Chromium	218.3	1,980	11.03
Iron	127.7	18,500	0.69
Aluminum	10.9	570	1.91
Sodium	33,000	37,000	89.19
Bismuth	201.8	26,000	0.78
Lanthanum	11.0	4,220	0.26
Silicon	571.8	5,670	10.08
Uranium	No measurement	3,550	---
Zirconium	0.8	4.0	20.00
Phosphate	15,600 (IC)	32,300	48.29
Sulfate	3,550 (IC)	3,680	96.47
Nitrate	41,300	Not Applicable	---
Fluoride	2,300	Not Applicable	---
TOC	3,120	Not Applicable	---
Radionuclides	($\mu\text{Ci/g}$)	($\mu\text{Ci/g}$)	
^{90}Sr	0.00097 (Grab)	5.41	0.018
^{137}Cs	0.087 (Grab)	0.166	52.33

Low-level and High-Level Vitrification Program

The final disposal option for Hanford Site wastes has been determined to be vitrification after partitioning into low-level and high-level fractions. This program has characterization needs in addition to those described for core sampling. The vitrification process will be performed after the solids have been pretreated. Therefore, the core sample information will provide preliminary bounding design conditions for the vitrification plant. Further characterization for technology development and regulatory compliance will be necessary on the pretreated waste that will be fed to the vitrification plant. Although the data requirements for this option are not formally defined, the analytical requirements for the previous Hanford Waste Vitrification program generally are applicable and are identified in the *Hanford Waste Vitrification Plant Feed Characterization Requirements*, Revision 4 (Wagner 1992). These requirements are quite similar to the pretreatment program requirements, and therefore are presented together in this section (see Table 6-2). For more specific information on a particular analyte not given in this table, consult the data package (McKinney, et al. 1993) or the appropriate table in Section 5.0.

The analytical program for vitrification not only entails determining if a waste type is suitable for disposal as glass, but also includes determining the physical and chemical characteristics of the glass for process-control purposes and to ensure regulatory compliance. Sampling and analysis plans will be developed on an individual basis for each tank or process batch. The characterization needs for these efforts include analyses for metals, water-soluble anions, radionuclides, semi-volatile organics, and rheological and physical testing for both the feed and vitrified product.

Tank 241-T-111 presently is not scheduled as an early feed for pretreatment and vitrification. The following characterization objectives need to be addressed in a data quality objective supporting the design of retrieval, pretreatment, and final disposal systems for early feed tanks:

- Provide extensive characterization of the chemical and radiological contents of the waste (solids and supernate) as it currently exists in the tanks to evaluate how it can be processed and to verify if the composition variability study envelope coverage for key analytes is adequate.
- Estimate the waste fraction that will remain after sludge wash pretreatment and estimate the feeds for the low-level and high-level streams for vitrification.
- Simulate sludge washing pretreatment on the waste material. This will provide a detailed understanding of the sludge wash process and obtain empirical data on soluble species removal.
- Determine the physical and rheological properties of the waste before and after simulated sludge washing to support the design of a waste retrieval system.

- Provide a supply of sludge washed material to be used as feed material for a laboratory scale vitrification.
- Satisfy the general characterization requirements for physical, chemical, and radiological analytes.

6.3.3 Waste Tank Safety Program Characterization Data Summary

Safety Screening

The tank safety screening data quality objective will be used to classify 149 SSTs and 28 double-shell tanks that contain high-level radioactive waste into specific safety categories for issues dealing with the presence of ferrocyanide, organics, flammable gases, and criticality (Babad and Redus 1994). The analytes used to make this classification are fuel energy value, total alpha concentration, weight percent moisture, and gas composition. The following table presents the analytes of concern, the criterion for classification, and the analytical result from the tank, where available. Further information on the tank contents are presented in subsequent sections. Because of the exothermic response of the waste material from the upper portions of tank 241-T-111, it has been placed on the Organic Watch List, and further studies trying to resolve the nature of the observed reaction are continuing. Table 6-3 provides a comparison of the tank values with the safety screening criteria.

Table 6-3. Tank 241-T-111 Comparison to Safety Screening Criteria.

Analyte	Safety issue/criteria	Tank result
Fuel energy value (cal/dry g)	Organics, ferrocyanide, flammable gas; -125 cal/dry g	Greater than -215 cal/dry g
Total alpha concentration	Criticality; 1 g ²³⁹ Pu/L	0.0053 g/L
Percent moisture	Organics, ferrocyanide, flammable gas; 17 wt%	76 wt%
Gas composition	25% lower flammability limit	NA

NA = Not available.

Criticality Safety

The criticality safety program has indicated that plutonium and uranium isotopic analyses on each core composite and the bottom six inches of each core is required to alleviate the concern for the potential of tank criticality. Therefore, upon extruding the last segment in a core, the waste to be tested shall be homogenized before a small aliquot is taken and analyzed for plutonium and uranium isotopic analyses by mass spectroscopy. The analyses will indicate whether the fissile species have settled in a concentrated layer at the bottom of a tank. However, this analytical criterion was established after the sampling and analysis of

tank 241-T-111 waste. Tables 6-4 and 6-5 present a summary of the core composite data for uranium and plutonium concentration. After reviewing the data, the isotopic analyses from both cores 31 and 33 were found to be very consistent with regard to composition, and the total alpha content indicated from the core 33, segment 9 homogenization data is extremely low (0.262 $\mu\text{Ci/g}$). Therefore further re-analysis and isotopic resolution of the core sample material from the lower portion of cores 31 and 33, segment 9 is not warranted. For this tank to exceed established operating limits for fissile material in the tank farms, a concentration of 1.58 $\mu\text{Ci/g}$ $^{239/240}\text{Pu}$ was calculated as a threshold limit value (Simpson 1994).

Table 6-4. Core Composite Uranium.

Core No.	U_{FL} (222-S) ($\mu\text{g/g}$)	U_{FL} (325) ($\mu\text{g/g}$)	^{238}U mass percent	^{235}U mass percent
Core 31, composite 1	2,180	4,000	99.3074	0.6755
Core 31, composite 2	3,880	5,200	99.3098	0.6761
Core 33, composite 1	3,180	4,500	99.3125	0.6761
Core 33, composite 2	1,950	3,500	99.3161	0.6717

FL = Uranium measurement by laser fluorimetry.

Table 6-5. Plutonium Concentration and Isotopic Distribution

Core number	Total Pu α (222-S) ($\mu\text{Ci/g}$)	Total Pu α (325) ($\mu\text{Ci/g}$)	^{238}Pu mass percent	^{239}Pu mass percent	^{240}Pu mass percent	^{241}Pu mass percent	^{242}Pu mass percent
Core 31 C1	0.138	0.628	0.005	96.7199	3.2109	0.0352	0.0151
Core 31 C2	0.136	0.565	0.0105	96.6351	3.2834	0.0496	0.0215
Core 33 C1	0.134	0.319	0.004	96.7540	3.1046	0.1071	0.0683
Core 33 C2	0.147	0.368	0.0105	96.5499	3.3436	0.0621	0.0337

Organic Tanks

The following characterization objectives support resolution of this unreviewed safety question and safety issue and support retrieval, pretreatment, and final disposal systems design. Table 6-6 provides a comparison of the tank core composite values with the Organic Data Quality Objective Criteria:

- Determine the overall waste energetics and properties governing waste reactivity behavior in the tanks.
- Determine the spatial distribution of ^{137}Cs and ^{90}Sr .

- Determine the concentration of TOC and the speciation of organics present in the waste.
- Satisfy the general characterization requirements for physical, chemical, and radiological analytes.

Table 6-6. Data Quality Objective Decision Limits for Organic Tanks. (Babad 1994)

Analyte	Decision threshold	Tank result
TOC (Dry wt%)	> 5 wt% (dry basis)	1.3 wt% (tank) 4.1 wt% (Core 33, Seg. 2)
Moisture content (wt%)	< 17 wt%	76 wt%
Presence of organic layer	Yes/No	No
Tank temperature (°C)	90 °C	16 °C
Total fuel content	-125 cal/dry g	In excess of -215 cal/dry g

Further analysis and secondary analytes for measurement were found to be unwarranted for the tank composites; however, the first two segments of core 31 and three segments of core 33 will undergo additional study. The results from this series of assays will be incorporated into the revision of this characterization report as they become available.

7.0 QUANTITATIVE/STATISTICAL INTERPRETATION OF THE DATA

This section contains the results of the statistical analysis of data from two core samples obtained from tank 241-T-111. Section 7.1 contains a description of the core-sample data used in the statistical analyses and some general observations regarding the data. Section 7.2 contains mean concentration estimates, and the associated 95 percent CIs, for each of the analytes in tank 241-T-111 waste. Section 7.3 contains estimates of the spatial variability (variability between cores), and estimates of the analytical error from the core composite data in tank 241-T-111. Further information can be found in Jensen et al. (1994).

Two types of analytical error were estimated from the core composite data: variability between composite samples within the same core and variability between the primary and duplicate analyses within each core composite sample. Estimates of the analytical measurement error were used to test the significance of the spatial and compositing variability. Spatial variability was significant (i.e., substantially greater than zero at the 0.05 significance level) in 40 out of 79 analytes in the tank. The compositing variance was significant for 38 out of the 79 analytes.

7.1 APPROACH

Cores 31 and 33 were the two valid core samples taken from tank 241-T-111. The segment recoveries for each core were given previously in Section 4. Two core composite samples were made for each core from the homogenized solid segment waste. Primary and duplicate results were obtained from each core composite.

The ICP acid digestion, ICP fusion dissolution, ICP water leach, IC water leach analyses, selected radiochemistry, and other GEA were performed on all composite core samples. These were the analytical results used in the statistical treatment of the data. In the tables in Jensen et al. (1994), the data are identified by the analysis method, the type of dissolution, and analyte; e.g., the notation ICP.a.AI refers to aluminum, acid digestion, and an ICP analysis. This document also contains the core composite sample results used together with ratios of the mean of each sample and duplicate divided by the detection limit for that pair. The data package for tank 241-T-111 (McKinney et al. 1993) contains a complete report of the sample results along with the laboratory quality control data. The core composite data for each analyte are illustrated in Jensen et al. (1994).

Statistics were calculated for analytes with concentrations greater than 10 times their detection limits (DL). Personnel within the TWRS Information Management Systems have identified a list of analytes that have exception to this rule. Table 7-1 lists the analytes specified. Statistics were calculated for the analytes from this list if the concentrations were greater than three times their DL. For a number of analytes, the concentrations of some samples were greater than a particular limit (3 or 10 times the DL), while the other samples were less than that limit. In these cases the statistics were calculated using all of the data

whether it was above or below the particular limit (3 or 10 DL). The above rules do not apply to alpha or beta/gamma counting methods. The ratios (mean/DL) reported in Jensen et al. (1994), are provided to show how large the analyte concentrations are relative to the DL.

Table 7-1. Special Analyte List.

Aluminum	Nitrate
Bismuth	Nitrite
Calcium	Phosphate
Chromium	Carbonate
Iron	Fluoride
Silicon	Chloride
Sodium	TOC
Zirconium	Cyanide

A close examination of those figures reveals several outlier data points in the core composite data:

- **ICP.a.Co** -- The primary result for core 31, composite 2 of 11.7 ug/g is over three times the duplicate result. The other results for ICP.a.Co all fall in the range 2.7 ug/g to 3.8 ug/g. The detection limit for ICP.a.Co is 0.8 ug/g.
- **ICP.a.Cu** -- The duplicate result for core 31, composite 2 of 127 ug/g is about four times the primary result of 31.7 ug/g. The detection limit for ICP.a.Cu is 0.4 ug/g.
- **NO₂** -- Both the primary and duplicate results from composite 2 of core 31 are about half the results for core 31, composite 1. The average of the results for core 31, composite one is 952 ug/g; the average for composite two is 525 ug/g. The detection limit for NO₂ by water digestion spectrophotometric analysis is 50 ug/g.

7.2 MEAN CONCENTRATION ESTIMATES

One of the tasks outlined as part of the waste characterization effort (Bell 1993, Winters et al. 1990a, Winters et al. 1990b), is to estimate the constituent inventories in the waste. The inventories are estimated by computing mean concentrations and 95 percent CIs on the mean concentrations for each constituent. The estimate of the inventory and CI on the inventory of an analyte in the tank are equal to the corresponding mean concentration estimates and CI multiplied by the volume of waste in the tank.

7.2.1 Statistical Methods

The concentration estimates are given in the form of 95 percent CIs on the mean concentration. It is assumed that each sample and its duplicate are analyzed independently of one another. The two analytical results are used to estimate the analytical measurement error. Because of the hierarchical structure of the data, the analytical measurement error alone is not the appropriate error term to use in computing the CIs. A linear combination of the analytical measurement variance and the spatial variance is the appropriate variance of the mean for the CIs. Jensen et al. (1994) contains a description of the statistical model and formulas used to calculate estimates of the mean, variance of the mean, and the CI on the mean.

7.2.2 Statistical Results

Table 7-2 contains the summary statistics by analyte for ICP acid digestion, ICP water leach, ICP fusion dissolution, IC, and selected radiochemical and physical analyses. The summary statistics are as follows:

- \bar{y} -- mean of the concentration data
- $\hat{\sigma}^2(\bar{y})$ -- estimated variance of \bar{y}
- df -- degrees of freedom
- 95% LL -- lower limit (LL) to the 95 percent CI on the mean
- 95% UL -- upper limit (UL) to the 95 percent CI on the mean.

For some analytes the lower confidence limit (95 percent LL) was negative. Because concentrations are greater than or equal to zero, any negative 95 percent LL values were set equal to zero.

The CIs in Table 7-2 are wide relative to the range of the data. The CIs are wide because only two cores were used to estimate the spatial variability. A minimum of two core samples is needed to estimate a tank's spatial variability.

7.3 COMPARISON OF THE VARIANCE COMPONENT ESTIMATES

Using the hierarchical structure of the core composite data, estimates of the between-core spatial variability, the compositing variability, and the analytical-measurement variability can be obtained. The spatial variance is a measure of the variability between cores. The compositing variance measures the variability between composite samples within the same core. The analytical-measurement variance is a measure of the difference between the analytical results from the sample and duplicate samples. This variance includes, among other things, the sample handling error and the chemical analysis error.

The estimate of the variance of the mean is a linear function of the spatial, compositing, and analytical-measurement variances. To help evaluate the magnitude of these three variance components, estimates of each variance component are given.

Table 7-2. Concentration Estimate Statistics. (3 pages)
 (Units $\mu\text{g/g}$ Except Radionuclides $\mu\text{Ci/g}$)

Analyte	\bar{y}	$\hat{\sigma}^2(\bar{y})$	df	95% LL	95% UL
ICP.a.Ag	1.26E+02	7.86E+03	1	0.00	1.25E+03
ICP.a.Al	5.41E+02	1.06E+04	1	0.00	1.85E+03
ICP.a.B	2.80E+01	7.56E+00	1	0.00	6.30E+01
ICP.a.Ba	6.90E+01	6.46E+01	1	0.00	1.71E+02
ICP.a.Bi	2.59E+04	6.38E+06	1	0.00	5.80E+04
ICP.a.Ca	1.88E+03	2.12E+05	1	0.00	7.72E+03
ICP.a.Cd★	5.80E+00	3.03E+00	1	0.00	2.79E+01
ICP.a.Co●	4.30E+00	1.63E+00	1	0.00	2.05E+01
ICP.a.Cr★	1.98E+03	1.63E+04	1	3.57E+02	3.60E+03
ICP.a.Cu	3.35E+01	3.53E+02	1	0.00	2.72E+02
ICP.a.Fe	1.85E+04	1.21E+06	1	4.55E+03	3.25E+04
ICP.a.K	1.14E+03	2.24E+03	1	5.34E+02	1.74E+03
ICP.a.La	4.22E+03	3.00E+05	1	0.00	1.12E+04
ICP.a.Mg	3.77E+02	6.36E+03	1	0.00	1.39E+03
ICP.a.Mn	6.33E+03	2.68E+04	1	4.25E+03	8.41E+03
ICP.a.Na	3.69E+04	1.56E+06	1	2.10E+04	5.27E+04
ICP.a.Ni	1.32E+02	5.12E+02	1	0.00	4.19E+02
ICP.a.P	1.03E+04	1.21E+05	1	5.90E+03	1.47E+04
ICP.a.Pb	3.47E+02	2.64E+04	1	0.00	2.41E+03
ICP.a.S	1.21E+03	1.06E+03	1	8.00E+02	1.63E+03
ICP.a.Si	4.69E+02	9.17E+02	1	8.40E+01	8.54E+02
ICP.a.Sr	3.00E+02	3.75E+02	1	5.39E+01	5.46E+02
ICP.a.Ti	1.95E+01	1.39E+02	1	0.00	1.69E+02
ICP.a.V	1.45E+01	6.58E+00	1	0.00	4.71E+01
ICP.a.Zn	6.50E+01	6.46E+02	1	0.00	3.88E+02
ICP.f.Ag	1.28E+02	8.05E+03	1	0.00	1.27E+03
ICP.f.Al	5.70E+02	9.70E+03	1	0.00	1.82E+03
ICP.f.Ba	6.46E+01	2.45E+01	1	1.73E+00	1.28E+02
ICP.f.Bi	2.36E+04	9.08E+06	1	0.00	6.18E+04
ICP.f.Ca★	2.42E+03	8.27E+04	1	0.00	6.07E+03
ICP.f.Cd★	8.12E+00	1.76E+00	1	0.00	2.50E+01
ICP.f.Cr	1.80E+03	1.56E+03	1	1.30E+03	2.30E+03

Table 7-2. Concentration Estimate Statistics. (3 pages)
(Units $\mu\text{g/g}$ Except Radionuclides $\mu\text{Ci/g}$)

Analyte	\bar{y}	$\hat{\sigma}^2(\bar{y})$	df	95% LL	95% UL
ICP.f.Cu	2.93E+01	3.56E+01	1	0.00	1.05E+02
ICP.f.Fe	1.80E+04	4.05E+06	1	0.00	4.36E+04
ICP.f.La	4.11E+03	3.08E+05	1	0.00	1.12E+04
ICP.f.Mg	3.55E+02	7.31E+03	1	0.00	1.44E+03
ICP.f.Mn	6.28E+03	1.88E+04	1	4.54E+03	8.02E+03
ICP.f.Na	3.70E+04	6.00E+06	1	5.82E+03	6.81E+04
ICP.f.Ni	8.14E+03	6.41E+06	1	0.00	4.03E+04
ICP.f.P	1.04E+04	8.42E+05	1	0.00	2.21E+04
ICP.f.Pb★	3.65E+02	9.38E+03	1	0.00	1.60E+03
ICP.f.S	1.23E+03	1.13E+04	1	0.00	2.58E+03
ICP.f.Si	5.67E+03	5.41E+04	1	2.71E+03	8.62E+03
ICP.f.Sr	2.98E+02	6.24E+01	1	1.97E+02	3.98E+02
ICP.f.Ti	4.79E+01	6.09E+02	1	0.00	3.62E+02
ICP.f.Zn★	1.06E+02	7.17E+00	1	7.22E+01	1.40E+02
ICP.w.Al●	1.09E+01	5.75E+00	1	0.00	4.14E+01
ICP.w.Bi	2.02E+02	2.40E+03	1	0.00	8.24E+02
ICP.w.Ca★	6.16E+01	3.32E+01	1	0.00	1.35E+02
ICP.w.Cr	2.18E+02	2.45E+01	1	1.55E+02	2.81E+02
ICP.w.Fe	1.28E+02	3.11E+02	1	0.00	3.52E+02
ICP.w.K	7.19E+02	1.54E+03	1	2.21E+02	1.22E+03
ICP.w.La★	1.10E+01	1.42E+01	1	0.00	5.89E+01
ICP.w.Mg★	3.64E+00	5.45E-02	1	6.75E-01	6.61E+00
ICP.w.Mn	2.47E+01	2.36E+01	1	0.00	8.65E+01
ICP.w.Na	3.30E+04	2.44E+06	1	1.31E+04	5.28E+04
ICP.w.P	5.68E+03	3.24E+04	1	3.39E+03	7.97E+03
ICP.w.S	1.15E+03	2.38E+03	1	5.29E+02	1.77E+03
ICP.w.Si	5.72E+02	5.35E+03	1	0.00	1.50E+03
IC.w.Cl ⁻	4.50E+02	1.11E+03	1	2.56E+01	8.74E+02
IC.w.F ⁻	2.30E+03	6.46E+05	1	0.00	1.25E+04
IC.w.NO ₂ ★	8.97E+02	2.10E+04	1	0.00	2.74E+03
IC.w.NO ₃ ⁻	4.12E+04	7.77E+06	1	5.82E+03	7.67E+04
IC.w.PO ₄ ³⁻	1.55E+04	1.53E+06	1	0.00	3.13E+04

Table 7-2. Concentration Estimate Statistics. (3 pages)
(Units $\mu\text{g/g}$ Except Radionuclides $\mu\text{Ci/g}$)

Analyte	\bar{y}	$\hat{\sigma}^2(\bar{y})$	df	95% LL	95% UL
IC.w.SO ₄ ²⁻	3.54E+03	2.85E+04	1	1.40E+03	5.69E+03
GEA.Am-241★	4.24E-02	2.61E-06	1	2.19E-02	6.29E-02
GEA.Co-60	3.64E-04	2.68E-10	1	1.56E-04	5.72E-04
GEA.Cs-137	1.66E-01	3.35E-03	1	0.00	9.02E-01
Gross.alpha	3.73E-01	1.96E-04	1	1.95E-01	5.51E-01
Gross.beta	1.51E+01	3.48E+01	1	0.00	9.00E+01
TGA.Percent.H ₂ O	7.65E+01	2.23E+01	1	1.64E+01	1.37E+02
NO ₂ ⁻	7.93E+02	8.76E+03	1	0.00	1.98E+03
Percent.H ₂ O	7.60E+01	5.81E-01	1	6.63E+01	8.57E+01
Pu-239/240	1.39E-01	9.19E-06	1	1.00E-01	1.77E-01
Sr-90	5.41E+00	3.53E+00	1	0.00	2.93E+01
TOC★	3.12E+03	3.83E+05	1	0.00	1.10E+04
Tc-99●	7.92E-03	8.90E-06	1	0.00	4.58E-02
U★	2.79E+03	2.01E+05	1	0.00	8.50E+03
pH	9.98E+00	7.79E-03	1	8.86E+00	1.11E+01

●: Analytes with a portion of the data below 3 times the DL.

★: Analytes with a portion of the data below 10 times the DL.

7.3.1 Statistical Methods

Estimates of the spatial variance ($\hat{\sigma}^2(S)$), compositing variance ($\hat{\sigma}^2(C)$), and analytical-measurement variance ($\hat{\sigma}^2(A)$), were obtained for each analyte using restricted maximum likelihood estimation methods. Restricted maximum likelihood estimation is discussed by Harville (1977).

To test the significance of the variance components, an analysis of variance (ANOVA) was calculated using the hierarchical statistical model described in Jensen et al. (1994). The mean square error terms in the ANOVA table were used to perform an F-test on the spatial variability and the composite variability. The p-values given in Table 7-3 were derived from the results of these tests.

Table 7-3. Variance Components Estimates. (3 pages)

Analyte	$\hat{\sigma}^2(S)$	Test: $\sigma^2(S)=0$ p-value	$\hat{\sigma}^2(C)$	Test: $\sigma^2(C)=0$ p-value	$\hat{\sigma}^2(A)$
ICP.a.Ag	1.56E+04	0.001	1.94E+02	0.000	3.16E+00
ICP.a.Al	1.89E+04	0.055	4.79E+03	0.000	1.06E+01
ICP.a.B	1.25E+01	0.093	9.28E-01	0.387	8.59E+00
ICP.a.Ba	6.91E+01	0.263	1.20E+02	0.000	3.54E-01
ICP.a.Bi	1.27E+07	0.000	6.25E+03	0.360	3.75E+04
ICP.a.Ca	4.10E+05	0.010	2.17E+04	0.074	9.95E+03
ICP.a.Cd★	5.96E+00	0.004	1.90E-01	0.039	5.34E-02
ICP.a.Co★	8.92E-01	0.376	8.08E-01	0.389	7.84E+00
ICP.a.Cr	3.17E+04	0.007	1.36E+03	0.081	6.75E+02
ICP.a.Cu	3.39E+02	0.290	1.67E+02	0.369	1.14E+03
ICP.a.Fe	2.33E+06	0.013	1.55E+05	0.063	6.25E+04
ICP.a.K	2.45E-24	0.911	8.86E+03	0.000	1.75E+02
ICP.a.La	5.91E+05	0.003	1.63E+04	0.019	2.88E+03
ICP.a.Mg	1.25E+04	0.005	5.18E+02	0.001	1.58E+01
ICP.a.Mn	2.97E+04	0.254	4.29E+04	0.030	1.00E+04
ICP.a.Na	2.76E+06	0.057	6.73E+05	0.016	1.05E+05
ICP.a.Ni	1.02E+03	0.000	6.13E+00	0.091	3.38E+00
ICP.a.P	2.37E-22	0.608	4.77E+05	0.000	1.25E+04
ICP.a.Pb	5.20E+04	0.003	1.41E+03	0.000	1.91E+01
ICP.a.S	1.11E+03	0.268	1.94E+03	0.003	1.25E+02
ICP.a.Si	2.57E-31	0.946	7.61E-14	0.418	7.34E+03
ICP.a.Sr	6.38E+02	0.079	2.18E+02	0.004	1.54E+01
ICP.a.Ti	2.75E+02	0.001	4.69E+00	0.000	7.83E-02
ICP.a.V	1.83E+00	0.423	2.25E+01	0.000	2.30E-01
ICP.a.Zn	1.22E+03	0.021	1.35E+02	0.008	1.42E+01
ICP.f.Ag	1.61E+04	0.000	6.23E+00	0.295	1.83E+01
ICP.f.Al	1.90E+04	0.005	6.78E+02	0.030	1.57E+02
ICP.f.Ba	3.99E+01	0.102	1.71E+01	0.012	2.19E+00
ICP.f.Bi	1.81E+07	0.001	2.88E+04	0.392	2.94E+05
ICP.f.Ca★	1.51E+05	0.008	2.07E-19	0.804	5.86E+04

Table 7-3. Variance Components Estimates. (3 pages)

Analyte	$\hat{\sigma}^2(S)$	Test: $\sigma^2(S)=0$ p-value	$\hat{\sigma}^2(C)$	Test: $\sigma^2(C)=0$ p-value	$\hat{\sigma}^2(A)$
ICP.f.Cd★	2.17E+00	0.126	1.21E-20	0.649	5.38E+00
ICP.f.Cr	3.72E-15	0.994	5.63E+03	0.013	1.21E+03
ICP.f.Cu★	6.97E+01	0.005	2.00E+00	0.119	1.43E+00
ICP.f.Fe	8.00E+06	0.003	1.68E+05	0.079	8.13E+04
ICP.f.La	5.96E+05	0.010	3.82E+04	0.012	4.98E+03
ICP.f.Mg	1.46E+04	0.000	5.15E-44	0.913	1.60E+02
ICP.f.Mn	1.66E-11	0.553	7.02E+04	0.011	9.70E+03
ICP.f.Na	1.17E+07	0.007	5.43E+05	0.044	1.65E+05
ICP.f.Ni	1.17E+07	0.033	4.18E-12	0.498	4.39E+06
ICP.f.P	1.57E+06	0.028	1.95E+05	0.049	6.45E+04
ICP.f.Pb★	1.85E+04	0.003	4.35E+02	0.030	1.02E+02
ICP.f.S	2.15E+04	0.017	2.00E+03	0.008	2.13E+02
ICP.f.Si	1.06E+05	0.005	1.00E+03	0.369	6.83E+03
ICP.f.Sr	6.12E-16	0.661	1.15E+02	0.222	2.69E+02
ICP.f.Ti	1.22E+03	0.000	2.66E-01	0.331	1.12E+00
ICP.f.Zn★	5.69E-23	0.440	1.10E-22	0.839	5.74E+01
ICP.w.Al●	7.35E+00	0.208	6.93E+00	0.061	2.72E+00
ICP.w.Bi	3.90E+03	0.102	1.30E+03	0.123	9.66E+02
ICP.w.Ca★	1.86E-11	0.144	1.69E-22	0.862	2.66E+02
ICP.w.Cr	5.66E-20	0.979	9.52E+01	0.001	5.62E+00
ICP.w.Fe	6.16E+01	0.436	9.05E+02	0.077	4.29E+02
ICP.w.K	2.28E+03	0.148	1.57E+03	0.001	4.73E+01
ICP.w.La★	2.71E+01	0.015	1.34E+00	0.226	2.23E+00
ICP.w.Mg★	3.04E-21	0.597	1.61E-01	0.098	1.14E-01
ICP.w.Mn	2.51E+01	0.266	3.19E+01	0.130	2.51E+01
ICP.w.Na	4.53E+06	0.030	6.84E+05	0.002	2.88E+04
ICP.w.P	3.98E+04	0.222	3.94E+04	0.089	2.13E+04
ICP.w.S	3.95E+03	0.091	1.50E+03	0.014	2.13E+02
ICP.w.Si	8.53E+03	0.113	1.98E+03	0.272	4.72E+03
IC.w.Cl	1.99E+03	0.043	1.15E-10	0.509	9.66E+02

Table 7-3. Variance Components Estimates. (3 pages)

Analyte	$\hat{\sigma}^2(S)$	Test: $\sigma^2(S)=0$ p-value	$\hat{\sigma}^2(C)$	Test: $\sigma^2(C)=0$ p-value	$\hat{\sigma}^2(A)$
IC.w.F ⁻	1.28E+06	0.001	1.37E+04	0.102	8.44E+03
IC.w.NO ₂ ⁻ ★	3.99E+04	0.015	5.22E-16	0.510	8.64E+03
IC.w.NO ₃ ⁻	1.42E+07	0.038	2.46E+06	0.013	3.44E+05
IC.w.PO ₄ ³⁻	2.59E+06	0.082	8.54E+05	0.030	1.99E+05
IC.w.SO ₄ ²⁻	5.27E+04	0.032	7.04E+03	0.071	3.14E+03
GEA.Am-241★	2.99E-32	0.786	8.13E-06	0.062	4.59E-06
GEA.Co-60	3.58E-10	0.046	5.14E-36	0.813	7.12E-10
GEA.Cs-137	6.61E-03	0.003	1.87E-04	0.000	1.88E-06
Gross.alpha	3.42E-04	0.065	7.74E-05	0.098	4.58E-05
Gross.beta	6.93E+01	0.000	3.14E-01	0.026	6.62E-02
TGA.%.H ₂ O	3.17E+01	0.008	3.78E-33	0.935	5.18E+01
NO ₂ ⁻	1.92E-14	0.789	3.46E+04	0.000	9.50E+02
Percent H ₂ O	8.99E-01	0.128	2.55E-01	0.259	5.46E-01
Pu-239/240	2.49E-28	0.736	2.01E-05	0.171	3.33E-05
Sr-90	7.04E+00	0.000	1.79E-02	0.209	2.61E-02
TOC★	6.10E+05	0.113	2.98E+05	0.006	2.72E+04
Tc-99●	1.76E-05	0.001	2.63E-07	0.027	5.75E-08
U★	6.24E-06	0.831	7.91E+05	0.001	2.99E+04
pH	7.11E-28	0.601	3.06E-02	0.001	1.19E-03

●: Analytes with a portion of the data below 3 times the DL.

★: Analytes with a portion of the data below 10 times the DL.

7.3.2 Statistical Results

The restricted maximum likelihood estimates of each component of variability along with the p-values (significance level) from the F-tests also are given in Table 7-3. P-values less than 0.05 indicate that $\sigma^2(S)$ or $\sigma^2(C)$ is significantly different from zero at the 0.05 significance level.

The p-values from the tests on $\sigma^2(S)$ were less than 0.05 for 40 out of the 79 analytes in tank 241-T-111 waste. Thus, for these 40 cases, differences between the results in the two cores were statistically significant**. The p-values from the tests on $\sigma^2(C)$ were less than 0.05 for 38 out of the 79 analytes in tank 241-T-111 waste. This indicates that, relative to the analytical error, differences between composite samples were significantly greater than zero in 38 cases. Conversely, for 41 out of 79 cases, differences between composite samples were not statistically significant. The number of analytes (and the amount that they contribute to the waste) for which $\sigma^2(S)$ and $\sigma^2(C)$ were statistically significant further suggests that the waste is heterogeneous.

7.4 MASS BALANCES

A method to help ensure the data are consistent and reasonable is to perform a mass and charge balance on the core composite sample data. This activity is a rough quality control check and provides insight to some of the properties of the matrix. To do this, the assumption in performing the mass balance is that the anions, cations, and water are all associated in some manner, but the exact chemistry of the association is not considered. Analytes contributing less than 0.2 weight percent, generally trace ICP analytes, AA analytes, and radionuclides, are considered negligible in this assessment. The assays that will contribute analytes to the mass balance are ICP acid or fusion (whichever gives higher quantitation), IC, TOC, and the gravimetric weight-percent water measurement.

Without considering the physical and chemical properties of the waste matrix and the context of the process history, the mass balances produced from these assays may be biased low. However, this bias is expected because it is known that there are analytes present that were not measured in the analysis of the samples. The IC anions only measure the water-soluble components; there is a substantial insoluble residue that must contain additional anions. Bias may be impacted substantially by chemical form, accountability, and variability in oxide or hydroxide content. Assumptions regarding the chemical combination of some of the analytes will be made and inserted into the mass/charge balance, presented in Table 7-4. Generally, this consists of assuming that some analytes are precipitated as an oxide or hydroxide, and that the shortfall indicated from the charge balance in microequivalent [$\mu\text{equ.}$] is present as one of those two analytes.

**Statistically significant for the purposes of this analysis means substantially greater than zero at the 0.05 level of significance.

Table 7-4. Core 31 and Core 33 Mass and Charge Balance. (2 pages)

Analyte	Core 31 average concentration ($\mu\text{g/g}$)	Core 31 charge ($\mu\text{equ/g}$)	Core 33 average Concentration ($\mu\text{g/g}$)	Core 33 charge ($\mu\text{equ/g}$)	Core 31/33 RPD
Ca^{+2}	2,710	135.50	2,140	107.00	23.51
Cr^{+3}	1,850	106.73	2,100	121.15	-12.66
Fe^{+2}	20,100	717.86	16,000	571.43	22.71
Mn^{+4}	6,160	448.00	6,400	465.45	-3.82
Na^{+}	39,400	1,713.04	34,600	1,504.35	12.97
Bi^{+3}	23,500	337.32	28,500	409.09	-19.23
La^{+3}	3,670	79.21	4,770	102.95	-26.07
Si^{+4}	5,900	842.86	5,440	777.14	8.11
U^{+6}	3,820	96.30	3,280	82.69	15.21
PO_4^{3-}	30,100	-950.53	31,700	-1001.05	-5.18
SO_4^{2-}	3,650	-76.04	3,460	-72.08	5.34
NO_3^{-}	44,100	-711.29	38,500	-620.97	13.56
F^{-}	3,110	-163.68	1,500	-78.95	69.85
TOC	3,740	-85.00	2,500	-56.82	39.74
Anion reconciliation					
O_2^{4-}	17,116	-2,139.50	16,926	-2,115.75	
OH^{-}	5,965	-350.88	3,325	-195.59	
Water content					
H_2O	735,000	0	790,000	0	-7.21
H_2O Calc.	785,109	0	798,859	0	-1.74

Table 7-4. Core 31 and Core 33 Mass and Charge Balance. (2 pages)

Analyte	Core 31 average concentration ($\mu\text{g/g}$)	Core 31 charge ($\mu\text{equ/g}$)	Core 33 average Concentration ($\mu\text{g/g}$)	Core 33 charge ($\mu\text{equ/g}$)	Core 31/33 RPD
Total	949,891	-0.10	991,141	0.05	
Percent difference*	-5.01		-0.89		

O_2^{4-} : Represents the overall mass and charge of oxygen added to manganese, uranium, silicon, TOC, and chromium as part of the assumptions given in Section 7.4. This notation is not meant to imply actual chemical form.

OH^- : Represents hydroxide amount calculated to reconcile charge balance

NOTE: Neither of these analytes (oxygen or OH^-) are analytically determined.

$$\text{Relative Percent Difference (RPD)} = \frac{\text{Core 31 value} - \text{Core 33 value}}{\left(\frac{\text{Core 31 value} + \text{Core 33 value}}{2} \right)} \times 100$$

*Percent difference is determined from a Total of $1.0\text{E}+06 \frac{\mu\text{g}}{\text{g}}$ i.e.,

$$\text{Percent Difference} = \frac{\text{sum of analytical values in a core} - 1,000,000}{1,000,000} \times 100$$

A significant source of error can be reduced by assuming all phosphorous is present as PO_4^{3-} . The water digestion ICP values for phosphorous (converted to PO_4^{3-}) and PO_4^{3-} values from the IC agree well. The ratio of soluble to insoluble phosphorous (taken as phosphate) indicates that it is only about 50 percent soluble. The process history of the tank also indicates that large amounts of phosphate were used to encourage precipitate formation. Therefore, an assumption that the phosphorus determined by ICP in the fusion acid/assay (and converted to phosphate) represents total PO_4^{3-} is not unwarranted. The phosphorus in the ICP fusion assay is converted to PO_4^{3-} and added to the other anions in the charge balance. This step will avoid double counting in the mass and charge balance calculations.

The following other assumptions will be made for the purposes of simplifying the calculations: manganese is assumed present as MnO_2 , uranium is present as $\text{UO}_2(\text{OH})_2$, silicon is present as SiO_2 , TOC as $\text{C}_2\text{O}_4^{2-}$, and chromium as Cr_2O_3 . These forms are not the only likely speciation of the analytes; however, the waste matrices are too complicated to represent every possible, or even probable compound present.

In the case of these waste materials, the disparity between the gravimetric water measurement and the TGA water content suggests (1) drying of the sample before the gravimetric assay; (2) incomplete drying during the gravimetric test, which biases the results low; or (3) one or more endothermic events occurring in the same temperature range (chemical reactions or phase transitions resulting in the loss of mass). One or more of these factors may be responsible for the observed trend. However, in this case, the analytical results and chemical assumptions that were made with regard to the waste matrix reconcile well.

7.5 SUGGESTED COMPONENTS OF WASTE MATRIX

The actual composition of the waste matrix is quite complex and trace amounts of various compounds probably exist in the tank. However, with some simple assumptions regarding how the anions and cations will combine, a list of the most probable compounds that exist in the waste matrix and contribute significantly to its overall makeup can be developed.

Table 7-5 is a condensed version of a more general chart found on page D-147 in the *Handbook of Chemistry and Physics 64th Ed.* (Weast 1984). It provides solubility data on some of the most common anions and cations. The oxidation state shown in the table for the cations is the most stable. However, precipitates may form for multivalent cations under varying conditions, and so precipitates are reported as likely, if conditions and anions in the assessment of the analyst warrant it.

Table 7-5. Probable Solids in the Waste Matrix.

	NO ₃	PO ₄ ³⁻	SO ₄ ²⁻	F ⁻	OH ⁻	Si (as SiO ₃ ²⁻)	Oxide 2	CO ₃ ²⁻
Bi ⁺³		PPT		PPT	PPT		PPT	
Ca ⁺²		PPT	PPT	PPT		PPT	PPT	PPT
Cr ⁺³		PPT	PPT	PPT	PPT		PPT	
Fe ⁺³		PPT		PPT	PPT		PPT	PPT
Na ⁺								
La ⁺³			PPT	PPT	PPT		PPT	PPT
Mn ⁺⁴		PPT		PPT	PPT	PPT	PPT	PPT
U ⁺⁶	NL	PPT	PPT	NL	PPT		PPT	

PPT = Precipitate forms.

NL = Precipitate formation not likely under tank conditions.

From the chromatographic data, suspected solubility behavior, and process information, chloride, nitrite, and carbonate will not be significant mass contributors to the waste matrix. Sodium, SO_4^{2-} , and NO_3^- are highly soluble, and thus probably do not contribute much to the insoluble solids. However, they contribute significantly to the overall solids content of the waste (dissolved + insoluble solids). Phosphorous is one of the most prevalent analytes, is approximately 50 percent soluble, and contributes substantially to both the soluble and insoluble solids. No analytical measurement of hydroxide was made for the solids (although there was an OH^- assay of the grab sample), but it is known that in the process history of tank 241-T-111, basic solutions were added routinely to the tank. The following are likely candidates for the insoluble solids:

- Bismuth phosphate, BiPO_4
- Bismuth fluoride, BiF_3
- Bismuth hydroxide, $\text{Bi}(\text{OH})_3$
- Bismuth trioxide, Bi_2O_3
- Calcium fluoride, CaF_2
- Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$
- Calcium carbonate, CaCO_3
- Calcium chromite, CaCr_2O_4
- Calcium oxide, CaO
- Calcium silicate, CaSiO_3
- Calcium sulfate, CaSO_4
- Calcium hydroxide, $\text{Ca}(\text{OH})_2$
- Chromium(II) fluoride, CrF_2
- Chromium(III) fluoride, CrF_3
- Chromium phosphate, $\text{CrPO}_4 \bullet 2\text{H}_2\text{O}$
- Chromium hydroxide, $\text{Cr}(\text{OH})_3$
- Chromium dioxide, CrO_2
- Chromium monoxide, CrO
- Chromium oxide, Cr_2O_3
- Iron(II) fluoride, FeF_2
- Iron(III) fluoride, FeF_3
- Iron(II) hydroxide, $\text{Fe}(\text{OH})_2$
- Iron(III) hydroxide, $\text{Fe}(\text{OH})_3$
- Iron(II) phosphate, $\text{Fe}_3(\text{PO}_4)_2$
- Iron(III) phosphate, FePO_4
- Lanthanum hydroxide, $\text{La}(\text{OH})_3$
- Lanthanum oxide, La_2O_3
- Lanthanum fluoride, LaF_3
- Manganese difluoride, MnF_2
- Manganese trifluoride, MnF_3
- Manganese phosphate, $\text{MnPO}_4 \bullet \text{H}_2\text{O}$
- Manganese hydroxide, $\text{Mn}(\text{OH})_2$
- Manganese dioxide, MnO_2
- Manganese oxide, Mn_3O_4

-
- Manganese(III) hydroxide, $\text{MnO}(\text{OH})$
 - Uranyl phosphate, $\text{UO}_2\text{HPO}_4 \bullet 4\text{H}_2\text{O}$
 - Uranyl hydroxide, $\text{UO}_2(\text{OH})_2$
 - Uranyl sulfate, $2(\text{UO}_2\text{SO}_4) \bullet 7\text{H}_2\text{O}$

Insoluble aluminosilicates are suspected of binding the ^{137}Cs . ^{90}Sr may be held by several possible insoluble ionic compounds. There are many more possible and complex compounds that conceivably could exist in the waste matrix. This list is not meant as authoritative or exhaustive, and the alkaline nature of the media may substantially alter the phase equilibria for some of these materials. However, it does provide a reasonable starting point for any further speciation work.

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8.0 CONCLUSIONS

Analyses of the waste show a very small number of analytes comprising a disproportionate majority of the waste. Water is the single largest analyte, making up over 75 percent of the solids mass. Less than one percent of the total mass of the tank waste is drainable liquid. Calcium, chromium, iron, manganese, sodium, lanthanum, bismuth, and silicon constitute approximately 10.7 percent of the solids mass. PO_4^{3-} and NO_3^- constitute approximately 7.4 percent of the total (i.e., soluble and insoluble) solids mass. The fraction of the total anions that nitrate and phosphate represent cannot be determined adequately because the analytical method measured only soluble anions and it is known that there are insoluble oxides and hydroxides that are not assayed at this time. The TOC was measured and found to be less than 1.3 weight percent (dry basis) in each core and for the tank as a whole. However, the TOC assay method is believed to be biased low for this waste matrix and individual segment results have been observed to be higher than the bulk value for the tank.

The only significant gamma emitter found in the waste was ^{137}Cs , and it was found at very low levels. No meaningful regional concentrations (hot spots) of radioisotopes or fuel were detected along the vertical axis in either core. The ^{137}Cs concentration was relatively constant between individual core composites and their replicates; however, the concentrations between core 31 and core 33 differed by a factor of 2. In addition, the ^{137}Cs concentration decreased by a factor of nearly 3 as a function of depth between segment 1 and segment 9 of core 33. The major source of radiological activity was ^{90}Sr , which was also at a very low level. The bulk waste temperature in the tank, obtained from a thermocouple tree, ranges between 16 to 20 °C (61 to 68 °F). The radiological activity of tank 241-T-111 waste material was quite low, ranging from 0.3 to 10 mR/hr, measured through the drill string. No significant radiological activity was found in the drainable liquid in the tank or in the water digestion of the samples, but radionuclides were liberated readily in the acid digestion sample preparation, as indicated from the homogenization data. This suggests that ^{90}Sr and ^{137}Cs are insoluble.

Cores 31 and 33 appear to have a T Plant process flush disposed on top of 224 waste, overlying a 2C waste heel. ^{241}Am and ^{137}Cs decrease substantially as a function of depth, thus their profiles nominally agree with fill histories, although individual batches and process upsets can show characteristics contrary to the general trend. These observations are consistent with the historical information regarding the transfer history, and the ICP element distribution through the segments. Discernable exothermic behavior was detected in the upper segments of both cores 31 and 33, even though the magnitude of the exotherms did not agree with the TOC present. This lack of an identifiable fuel source was attributed to the inability of the persulfate oxidation method to adequately quantitate TOC in this waste matrix. Another hypothesis under investigation is the potential contribution of an exothermic inorganic reaction that has not been identified.

Historical data indicated that 2C and 224 wastes were not expected to give any exothermic response at all, and could not create a propagating hazard. This prediction has been upheld for 2C wastes as no exotherms were observed. In the 224 wastes, even though some small amounts of oxalate were indicated in the flowsheets, no reaction was expected. Calculations of the bulk waste inventory and inventories for several analytes of interest to the various safety issues [organics (as TOC), NO_3^- , ^{137}Cs , ^{90}Sr , plutonium, and water] were made. The calculated TOC by weight percent was smaller than the watch list criterion on a bulk basis, but the energetics results do not reconcile well with that interpretation, and indicate that the organic content in the tank may be disproportionately partitioned between the upper 100 cm of waste and the remainder of the tank. However, it is important to note that the organics concentration, even in this hypothesized enriched layer, may be too low to support a self-sustaining reaction in its present state. Reactions were observed only after all water had been removed from the waste matrix, and water makes up over 75 weight percent of the waste, providing an enormous heat sink to be overcome before reactions can be initiated. Both the historical and analytical data from tank 241-T-111 strongly indicate that the waste lacks the fuel concentration needed to sustain any propagating exothermic behavior or a heat source intense enough to trigger a reaction. None of the other calculated bulk inventory values exceeded any level of concern (see Table 8-1).

Table 8-1. Comparison of Tank 241-T-111 Analyte Values to Safety Issue Criteria.

Analyte	Safety issue criteria ¹	Calculated/measured value
ΔH (dry basis)	-75 cal/g	In excess of -215 cal/g
$^{239/240}\text{Pu}$	50 kg	9.2 kg
Temperature	300 °F (149 °C)	16 °C (60.5 °F)
Heat load	11.72 kw	0.08 kw
Organic content (TOC, Dry basis) (10% sodium acetate equivalent)	3.0 wt% TOC	1.3 wt% TOC (This result is likely biased low)

¹(Lindsey 1986, RHO 1988, Boyles 1992, Reep 1992)

Experimental and analytical evidence from tank 241-T-111 waste suggests the risk from organic compounds in this particular Hanford Site high-level waste tank is acceptable and that a propagating exothermic reaction under current and near-term tank operating conditions is not credible.

8.1 RECOMMENDATIONS

The following recommendations are made based on the data and analyses presented in this report and the goals of the characterization effort:

- Investigate the potential existence of alternate transfer paths from T Plant.
- Examine more closely the chemical behavior, reactivity, and composition of Turco decontamination agent.
- Continue to characterize tank 241-T-111 sample matrices at PNNL.
- Investigate the possible kinship between tank 241-T-111 and other tanks.
- Research and develop improved assay methods for TOC.
- Investigate observed discrepancy for alpha-emitting radionuclides (especially ^{239/240}Pu and U).

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